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FUNDAMENTAL PROPERTIES OF TAILINGS SLUDGE FROM THE HOT WATER EXTRACTION OF OIL SANDS

Final Report

by

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FUNDAMENTAL PROPERTIES OF TAILINGS SLUDGE FROM THE HOT WATER EXTRACTION OF OIL SANDS

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EXECUTIVE SUMMARY

The objective of the present work was to examine some fundamental properties of a sludge to determine reasons for its stability. A number of studies including particle size analysis, mineral analysis, rheology and long term settling were carried out on the whole sludge. The solids portion of the sludge was also treated with a series of organic solvents to remove organics or modify the solid surfaces, and studies carried out on both the residual solids and some of the extracts.

The present report is divided into four volumes. Volume I focusses on some of the analyses of whole sludge and of its parts. The solids content is 28 wt%, with 90% of these solids being less than 37 μ. X-ray diffraction indicated that quartz, kaolinite and illite predominate. The water chemistry is dominated by dissolved NaCl and $NaHCO_3$ at pH 8. Rheological data suggest that the sludge has a structure dependent upon its shear history. Addition of NaCl to the sludge results in flocculation and a large strengthening of the structure as indicated by a large overshoot stress obtained from the rheological curves. Between 0.08 and 0.12 M salt concentration the sludge appears to be at its maximum destabilization point. Following treatment with a number of organic solvents the redispersed solids exhibited enhanced settling properties. None of the techniques of total organic carbon analysis, infrared, thermogravimetric analysis or x-ray diffraction, could distinguish between the solvent treated solids to explain the settling differences.

In Volume II is discussed the settling properties of whole sludge since settling is a basic criterion of sludge stability. Experiments showed that care must be taken when sampling sludge to determine settling rates, since the previous history of the sludge is important. It was shown that the concentration of the aggregates in sludge which impart structure may be reduced by dilution, but that the size and shape of the aggregates does not change. The much enhanced settling rate of the redispersed solids which had been treated with methanol points to a connection between multivalent ions and humic materials.

The results obtained using electrokinetic analysis are discussed in Volume III. No correlation was found between zeta potential and settling rate for all solids that had been extracted with organic solvents. It was found, however, from studies with kaolinite that some surface active agent in the sludge water can change the electrokinetic properties of the solid/water interface and possibly change settling properties. Furthermore, some indication of the changes at the interface may be found by studying the potentiometric titration curves.

Volume IV discusses the extraction and characterization of humic substances from oil sand solids from which the bitumen had been removed using toluene/iso-propyl alcohol solvent. An extraction efficiency of only 3.3 % was achieved due to the strong binding between these organics and the clay minerals. The

carbon content of the humic material (65 %) is higher and the oxygen content (21 %) is lower than that reported for most soil extracted humic acid. Infrared scans indicated that this material is similar to the humic material obtained from oil sand feed. Nuclear magnetic resonance indicated a 50 % carbon aromaticity, and showed the presence of carboxylic, carbonyl and carbohydrate carbon. The binding of both the extracted and a commercial humic acid to both kaolinite and cleaned sludge solids was studied. Desorption experiments were attempted, but were not successful due to the very strong binding.

Finally, Volume V contains two appendices which list all of the settling experiments and provide a discussion of some of the experiments. By reference to the list all the actual data may be found on disk at the Alberta Research Council.

INTRODUCTION

One of the major problems in the exploitation of mineable oil sands using the hot water process is the ultimate disposal of the tailings. This stream is an aqueous suspension of sand, clays and bitumen at a pH of between 8 and 9. The clays present in the tailings consist principally of kaolinite and illite. The basic problem is the large volume of sludge which remains even after long term settling in the tailings pond.

Various types of dissolved and clay-associated organics are present. The organics include carboxylic and sulphonic acids (1-3). Both of these classes of compounds, which are generated by the addition of sodium hydroxide to the process, aid in the extraction of bitumen. However, these same surfactant properties adversely affect the settling of clays in the sludge (4).

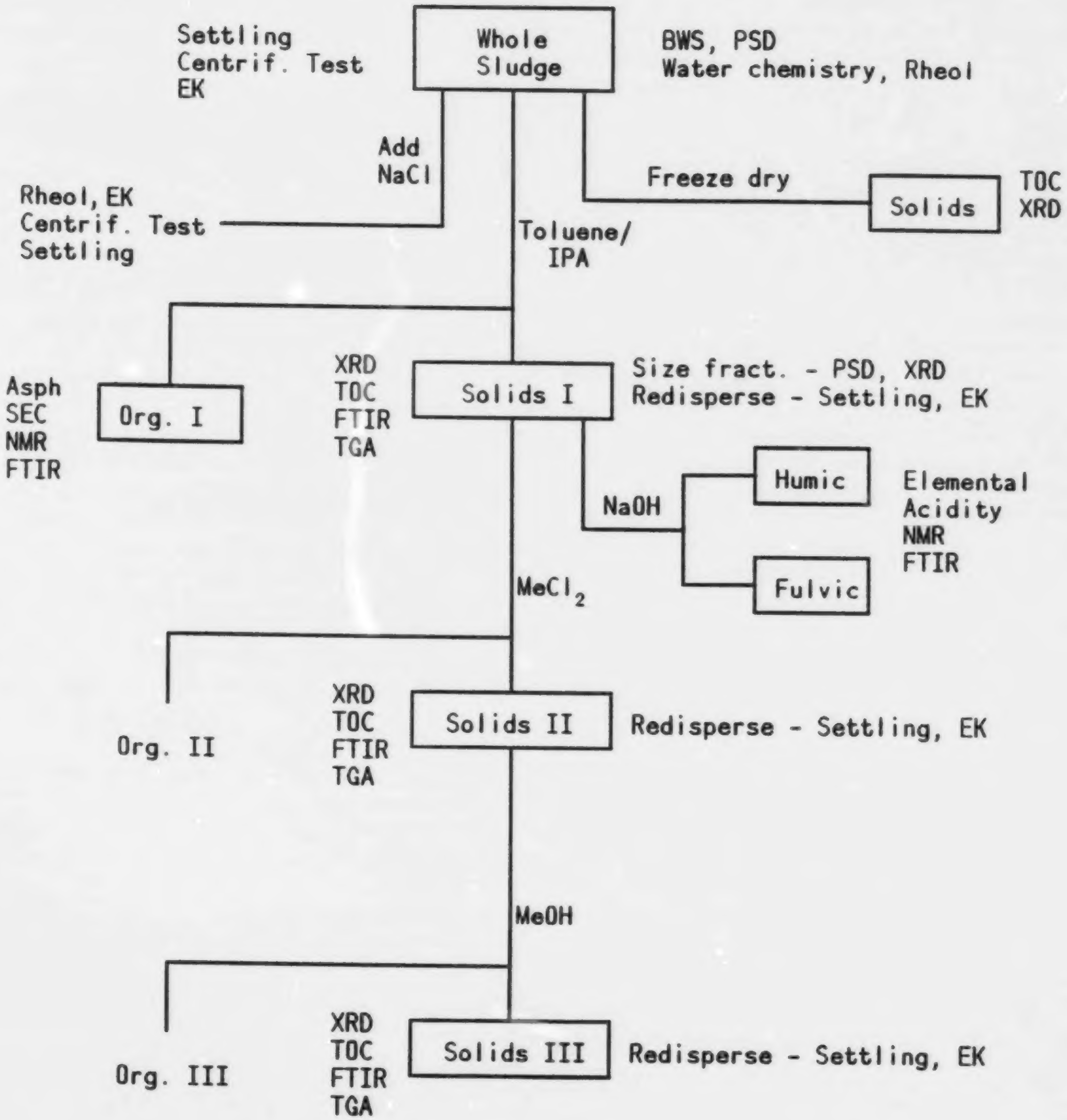
Several authors have shown that soluble organic surfactants disperse clay particles in the sludge and create a stable suspension (2, 5-7). A stable dispersion could also be formed as a result of repulsive forces due to the high negative surface charges on the clay particles (8-12). It is also possible that bound organics on the clay particles may link with bitumen in the tailings and help create a stable suspension, thus reducing the ability of the sludge to consolidate (13-16). A number of treatments, including chemicals, geotechnical methods, and process modifications have been proposed as solutions to the sludge problem. None has been commercially developed because of high operating costs.

The objective of the present work was to examine some fundamental properties of a sludge in order to determine the reasons for its stability. This was accomplished by studying the properties not only of whole sludge, but also of its constituent parts as indicated in Figure 1. A number of studies including particle size analysis, mineral analysis, rheology and long term settling were carried out on the whole sludge. The solids portion of the sludge was treated by a series of organic solvents in order to remove organics or otherwise modify the solid surfaces, and studies were carried out on both the residual solids and some of the extracted organic materials as shown in Figure 1.

The present report is divided into five volumes. Volume I focusses on some of the properties of whole sludge such as bitumen, water and solids content, particle size distribution, water chemistry, rheology and mineral analysis. These are important properties in the definition of any sludge. Also considered in this section are properties, and a characterization of the residual organic material on the solvent extracted solids. Volume II discusses the settling properties of the whole sludge, since settling is a fairly basic criterion of sludge stability. The effects of dilution, ionic strength and of modification of the solid surfaces by solvent treatment are also considered in this volume. The latter study was carried out by redispersion of the solids in water. The third volume focusses on the use of electrokinetic analysis in

FIGURE 1

An Overview of the Properties of Tailings Sludge Study



EK = electrokinetic analysis; **BWS** = Bitumen, water, solids determination;
Rheol = rheology studies; **PSD** = particle size distribution;
XRD = x-ray diffraction; **TOC** = total organic carbon;
FTIR = Fourier transform infrared; **TGA** = thermogravimetric analysis;
Asph = asphaltene determination; **SEC** = size exclusion chromatography;
NMR = nuclear magnetic resonance.

defining the stability of sludge, and in determining the effects of organics both in the sludge water and adsorbed onto the solid surfaces. Volume IV goes into the details of extraction and characterization of the tightly bound organic material, humic and fulvic acids, which may influence the stability of sludge. The readsorption of this material onto the cleaned sludge solids and kaolinite was also studied to learn more about organic-clay interactions. Finally Volume V contains two appendices. The first is a list of all settling experiments, for which the actual data may be found on disk at the Alberta Research Council, Clover Bar. The second appendix is a progress report on this project from March 1989, which contains a large amount of actual settling data.

REFERENCES

1. Ali, L.H., Fuel **57**(1978)357.
2. Hockins, M.B. and Lee, G.W., Fuel **56**(1977)325.
3. Schramm, L.L. and Smith, R.G., Proc. 35th Can. Chem. Eng. Conf., Calgary, Vol. 1 (1985)189.
4. Speight, J.G. and Moschopedis, S.E., Alberta Research Council Information Series 86 (1986).
5. Erskine, H.L., "Separation of Clay and Mineral in Heavy Oil Production", in The Future of Heavy Crude and Tar Sands, Meyer, J.C. et al. Eds. (1982)519.
6. Moschopedis, S.E., Fryer, J.F. and Speight, J.G., Fuel **56**(1977)109.
7. Levine, S. and Sanford, E., Proc. 30th Can. Chem. Eng. Conf., Edmonton, Vol. IV: Oil Sands, Coal and Energy Modelling, Wanke, S.E., Ed. CSChE Publications (1980)1112.
8. Young, R.N. and Sethi, A.J., J. Can. Petrol. Technol. **17**(1978)76.
9. Srinivan, N.S., Spitzer, J.J. and Hepler, L.G., J. Can. Petrol. Technol. **21**(1982)25.
10. Hall, E.S. and Tollefson, E.L., AOSTRA J. Res. **1**(1984)43.
11. Schultz, K.F. and Morrison, D.N., Alberta Research Council Open File Report **1973-8**(1973)10.
12. Lane, S., Preprints, 34th Annual Meeting of Petroleum Society of CIM, Paper No. 83-34-33(1983).
13. Kessick, M.A., Int. J. Mineral Proc. **6**(1980)277.
14. Kessick, M.A., Clays and Clay Minerals **27**(1979)301.
15. Kratochvil, B., Maitra C., Montgomery, D.S. and Strausz, O.P., AOSTRA J. Res. **2**(1985)59.
16. Kessick, M.A., J. Can. Petrol. Technol. **18**(1979)49.

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VOLUME I

ANALYSES OF SLUDGE AND EFFECTS OF SALT AND ORGANICS ON ITS PROPERTIES

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ANALYSES

Sampling

The properties of hot water extraction tailings sludges will vary greatly depending upon the processing conditions and the sampling location. It was decided at the beginning of this study that a particular sludge would be subsampled and used in all the experiments carried out.

The sludge employed was a batch of 2000 gallons recovered from the Syncrude tailings pond in August 1986, and stored in an indoor tank at Syncrude Research. Prior to sampling, the contents were circulated for 24 h during which time air was entrained which resulted in some bitumen flotation. As a result the six five-gallon samples which were taken may be somewhat low in bitumen content. All samples were then filtered through a 250 μ screen to remove pieces of wood, roots and oil globs, in order that they would be as homogeneous as possible.

Bitumen-Water-Solids Analysis

Subsamples from the preceding six sample pails gave the bitumen-water-solids results shown in Table 1. A modified Dean Stark method with toluene solvent was used. These subsamples were obtained by vigorously stirring the contents of each pail and removing sludge with a large soup ladle. As seen from the results in Table 1 most samples analyzed within a fairly narrow range, indicating a satisfactory homogenization procedure. The mean solids content is 28.4 wt%.

Particle Size Distribution

A sludge sample was treated with several successive batches of a toluene and iso-propyl alcohol (IPA) solution (50/50 by volume) followed by centrifugation in order to remove the water and bitumen. The particle size distribution of these solids was determined in two ways, by Microtrak and by sieving followed by Coulter Counter. The results are listed in Table 2. It can be seen that the latter method gives a higher distribution at the smaller size end. Since the Coulter Counter is known to better represent samples with a significant portion of the small particle sizes, this method is assumed to be more accurate and essentially indicates that about 30 wt% of the solids is in the clay size range (< 2 μ), and that 88 wt% is <37 μ.

X-Ray Diffraction Analysis

In order to define mineralogically the solids contained in the -37 μ fraction of the sludge sample, an x-ray diffraction (XRD) study was carried out. From this size fraction, which comprised about 90 wt% of the

TABLE 1: Bitumen Water Solids Analyses of Sludge Samples

	Weight Percentage		
Pail #	Bitumen	Water	Solids
1	1.95	70.55	27.50
2	2.10	67.30	30.60
3	1.95	68.80	29.20
4	1.75	70.95	27.30
5	1.85	70.55	27.60
6	1.85	70.22	27.95
Mean ± Std. Dev.	1.91 ± 0.12	69.73 ± 1.40	28.36 ± 1.29

TABLE 2: Particle Size Distribution of Sludge Solids by Sieve and Coulter Counter, and by Microtrak

Size (μm)	Cumulative Weight %	
	Sieve and Coulter	Microtrak
177.0	0.7	
150.0		1.1
125.0	2.4	
88.0	5.0	2.2
62.5	7.4	3.1
44.0	10.4	6.1
37.0	11.9	
31.0		12.2
22.0		16.1
20.2	12.4	
16.0	14.3	23.6
12.7	17.4	
11.0		32.5
10.1	21.9	
8.0	27.2	
7.8		41.6
6.3	33.0	
5.5		51.3
5.0	40.4	
4.0	47.9	
3.9		64.0
3.2	55.9	
2.8		75.8
2.5	63.5	
2.0	70.4	
1.9		87.3
1.6	78.0	
1.4		95.2
1.3	84.7	
1.0	90.8	
0.8	95.5	
0.6	100.0	

solids, a series of smaller size fractions were prepared by a number of settling and centrifugation steps.

The XRD work was carried out by Fred Longstaffe (1). Samples were packed into aluminum sample holders, and analyzed using Cu K-α radiation at 30 kV and 25 mA from 2 to 82 degrees two-theta. The diffractogram of fraction 1 (nominal 11 to 38 μ size range) is shown in Figure 1. The lower trace is scaled to full intensity of the largest peak; the upper trace is an expansion to facilitate study of less intense peaks. A semi-quantitative analysis for this sample is given in Table 3. The percentages are normalized, weighted peak heights, and only represent approximations of the true weight percentage of each phase. The actual particle size distribution of fraction 1 as determined by Coulter Counter is shown in Figure 2.

The diffractograms of each of the other size fractions and their size distributions as determined by Coulter Counter are shown in Figures 3 to 10. As seen in Table 3, with decreasing particle size the relative abundance of illite and kaolinite increased while that of quartz decreased. The relative abundances of feldspars and carbonate minerals remained approximately constant, except in the very finest size fraction where these phases were absent. The relative abundance of illite versus kaolinite increased markedly in the finest size fraction examined.

A attempt was made to assess putative variations in clay mineral crystallinity. Two functions, 10A-Xtal and 7A-Xtal were defined as:

$$\frac{\text{peak height of (001) diffraction}}{\text{peak width at half height of the (001) diffraction}}$$

for illite and kaolinite respectively. Higher values reflect an increase in peak sharpness, and hence an increase in crystallinity. The results in Table 3 indicate a systematic decrease in both with decreasing particle size as would be expected. The deterioration in illite crystallinity reflects the changing character of the illite as well as its decreasing particle size. The illite (001) diffraction shows progressively greater low-angle asymmetry with decreasing particle size. This behavior results from the increasingly more degraded nature of the illite, as described for clay minerals associated with Athabasca asphaltene by Ignasiuk et al. (2). Degraded illites are generally characterized by decreased potassium contents and the development of hydroxy islands between layers near crystal edges that can cause the clay to become partly expandable in the presence of water or organic liquids or vapors.

Water Chemistry

Water was separated from a sample of sludge by centrifugation followed by 0.45 μ filtration. Cation analysis was carried out by inductively coupled plasma (ICP), and anion analysis by ion chromatography (IC). The total organic and inorganic carbon values were carried out on a total carbon analyzer. The

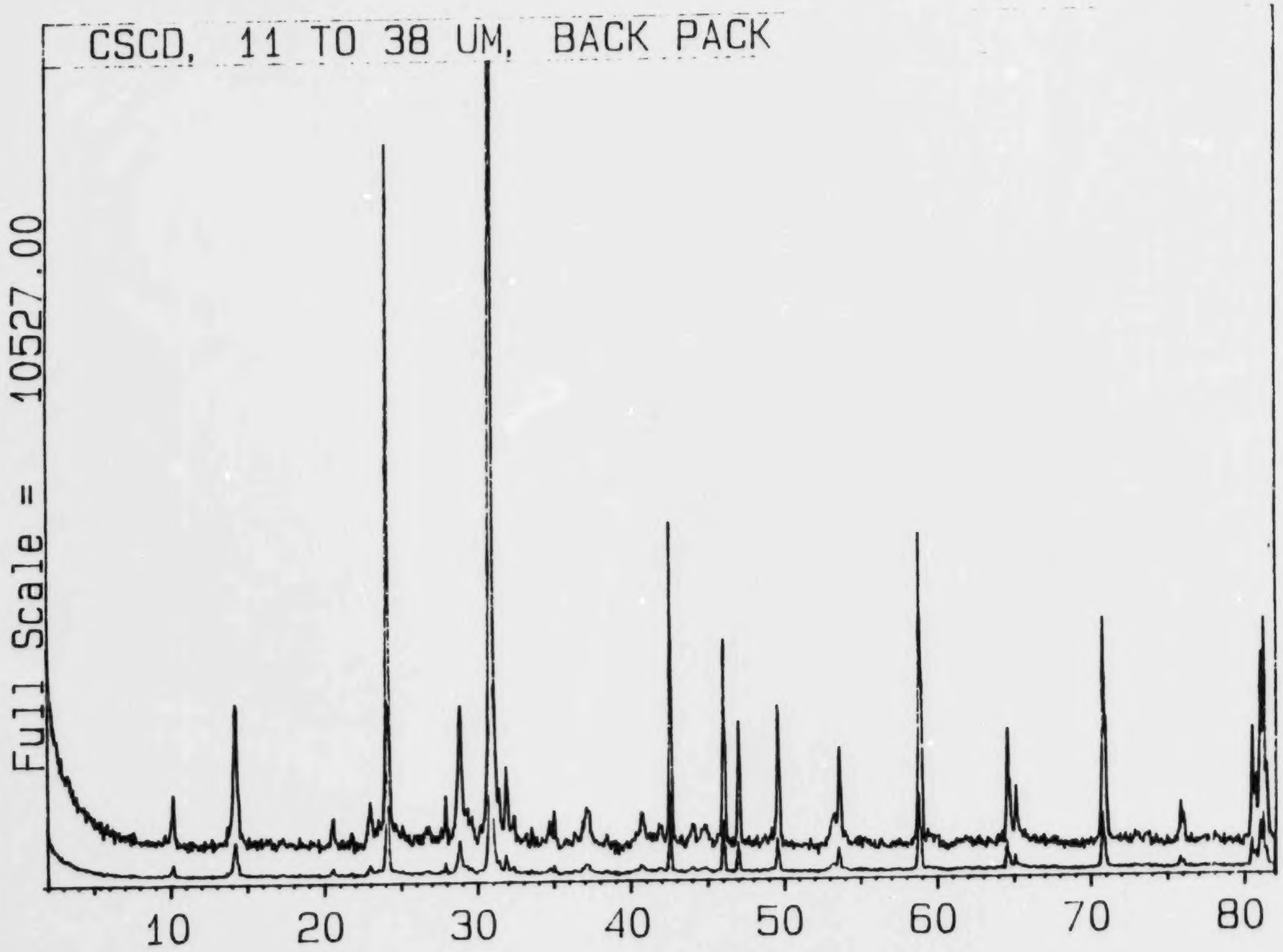


FIGURE 1: Diffractogram of sludge solids fraction 1

TABLE 3: Semi-quantitative X-Ray Diffraction Analysis of Sludge Solids Size Fractions

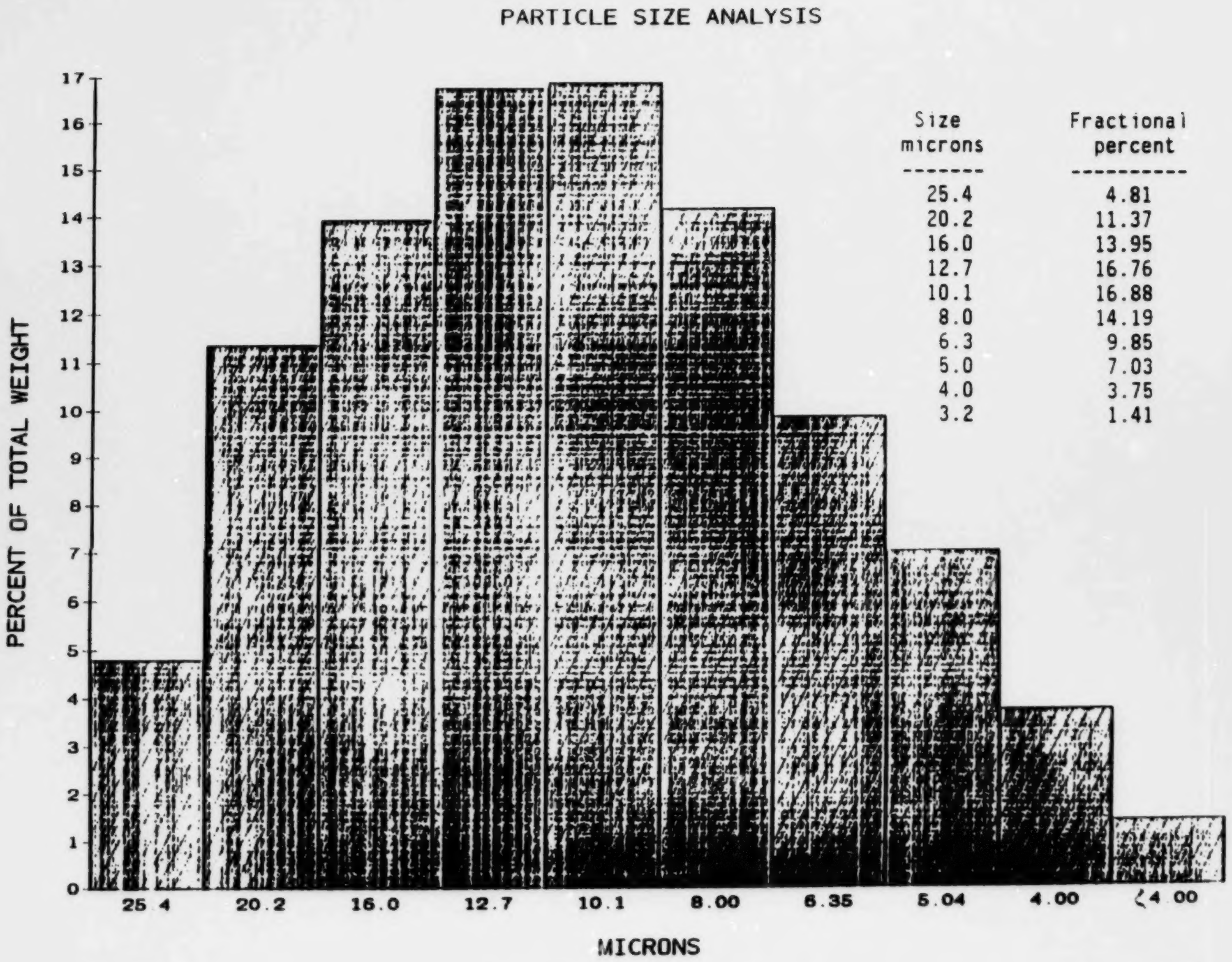
Fraction***	I	K**	Qtz	KF	PI	Sid	Cal	10Å-Xtal	7Å-Xtal
1	2.9%	4.4%	88.0%	1.9%	0.7%	1.3%	0.8%	12.00	28.00
2	4.7%	10.8%	77.7%	1.2%	1.7%	2.5%	1.4%	9.50	29.00
3	5.2%	15.5%	71.1%	1.6%	1.9%	2.9%	1.9%	7.20	30.57
4	10.3%	32.1%	48.7%	2.3%	2.0%	2.6%	2.0%	2.77	24.89
5	44.4%	37.0%	18.5%	0.0%	0.0%	0.0%	0.0%	0.78	3.75

I = illite; K = kaolinite; Qtz = quartz; KF = K-feldspar; PI = plagioclase; Sid = siderite; Cal = calcite; 10A-Xtal = measure of crystallinity of illite; 7A-Xtal = measure of crystallinite of kaolinite.

* Values reported are weight peak heights only, not weight percent.

** Includes minor chlorite and/or berthierine.

*** Actual size distributions of these fractions are given in Figures 2, 4, 6, 8 and 10.



Size microns	Fractional percent	Cumulative percent
25.4	4.81	4.81
20.2	11.37	16.18
16.0	13.95	30.13
12.7	16.76	46.89
10.1	16.88	63.78
8.0	14.19	77.96
6.3	9.85	87.81
5.0	7.03	94.84
4.0	3.75	98.59
3.2	1.41	100.00

FIGURE 2: Sludge solids fraction 1

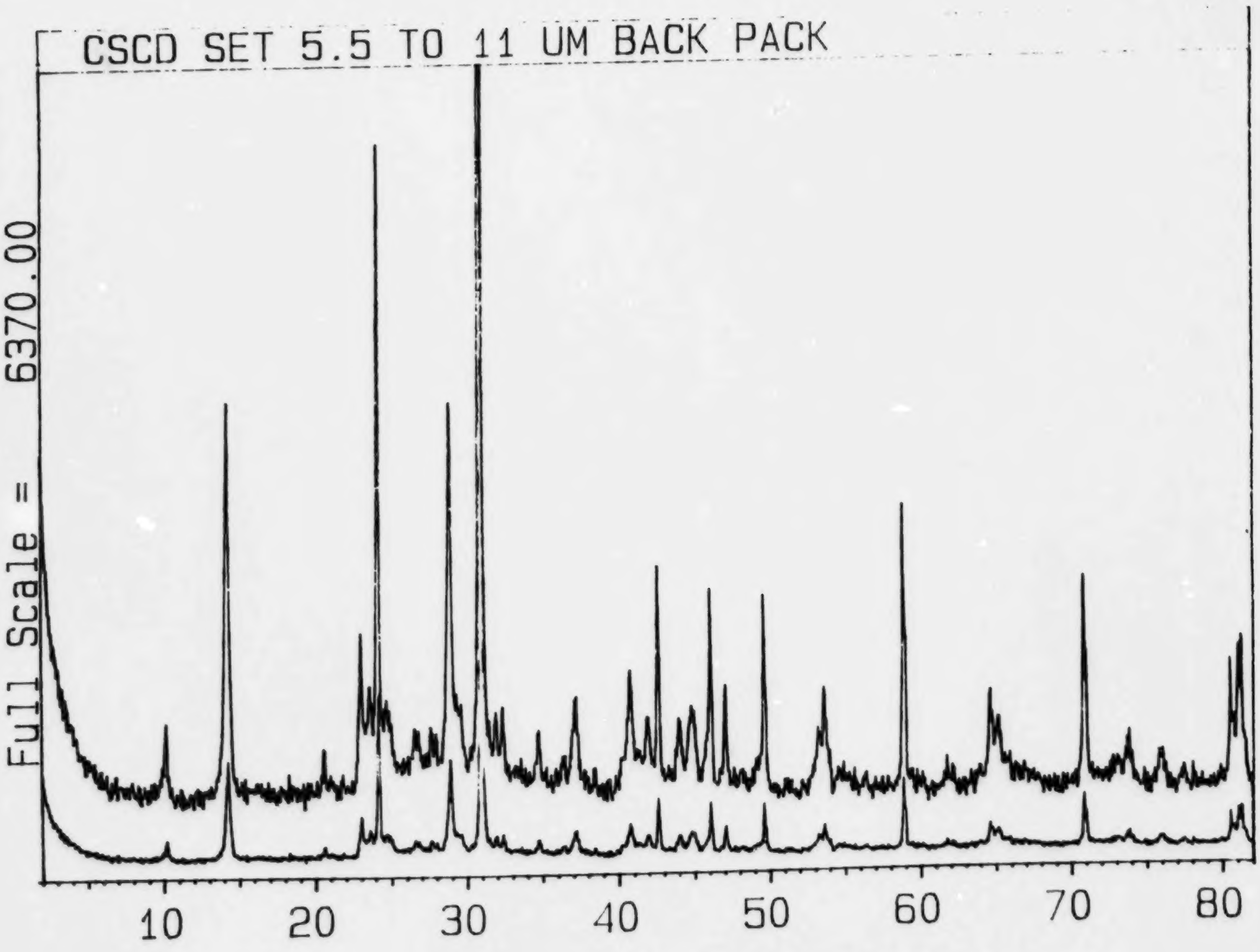
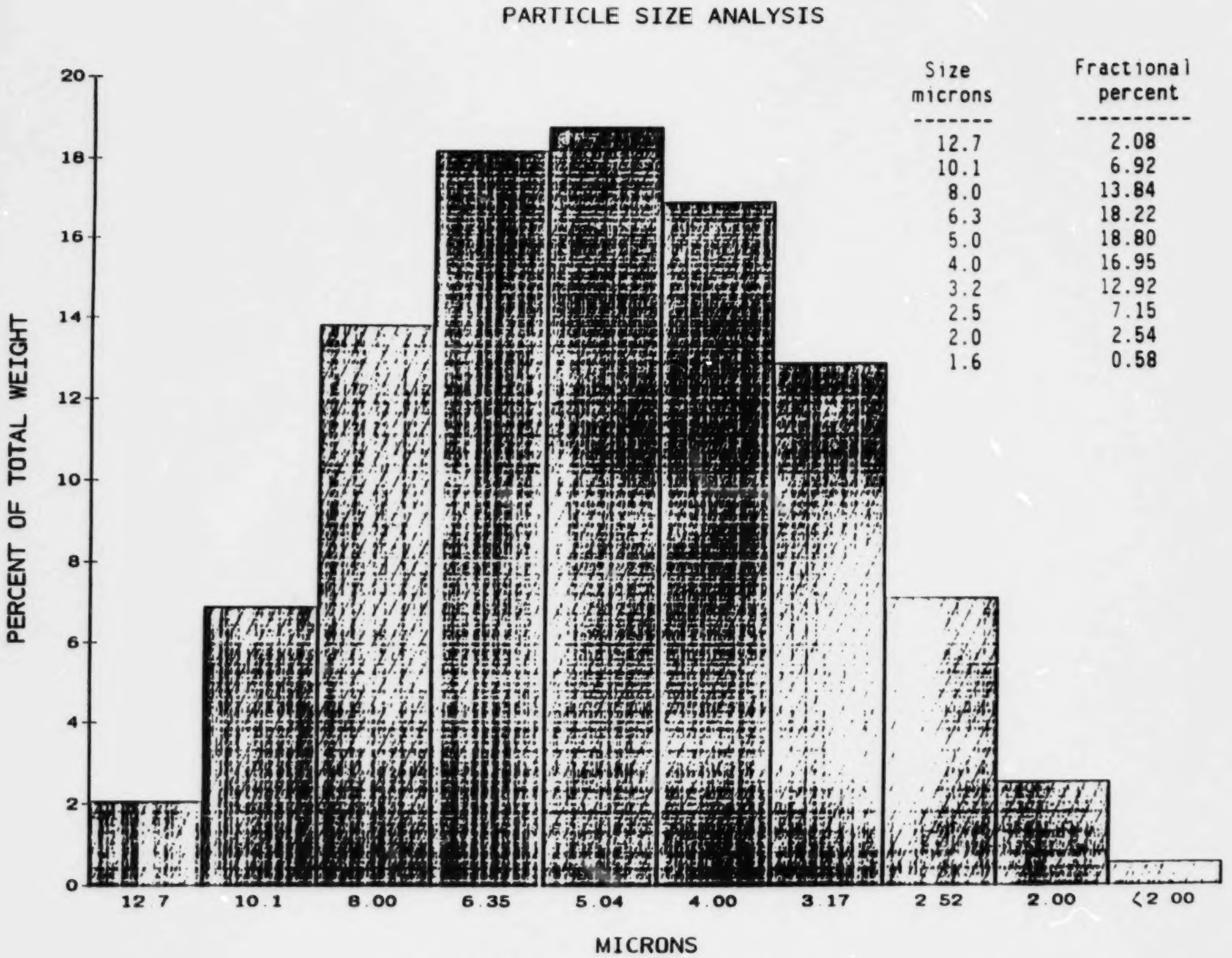


FIGURE 3: Diffractogram of sludge solids fraction 2



Size microns	Fractional percent	Cumulative percent
12.7	2.08	2.08
10.1	6.92	9.00
8.0	13.84	22.84
6.3	18.22	41.06
5.0	18.80	59.86
4.0	16.95	76.82
3.2	12.92	89.73
2.5	7.15	96.89
2.0	2.54	99.42
1.6	0.58	100.00

FIGURE 4: Sludge solids fraction 2

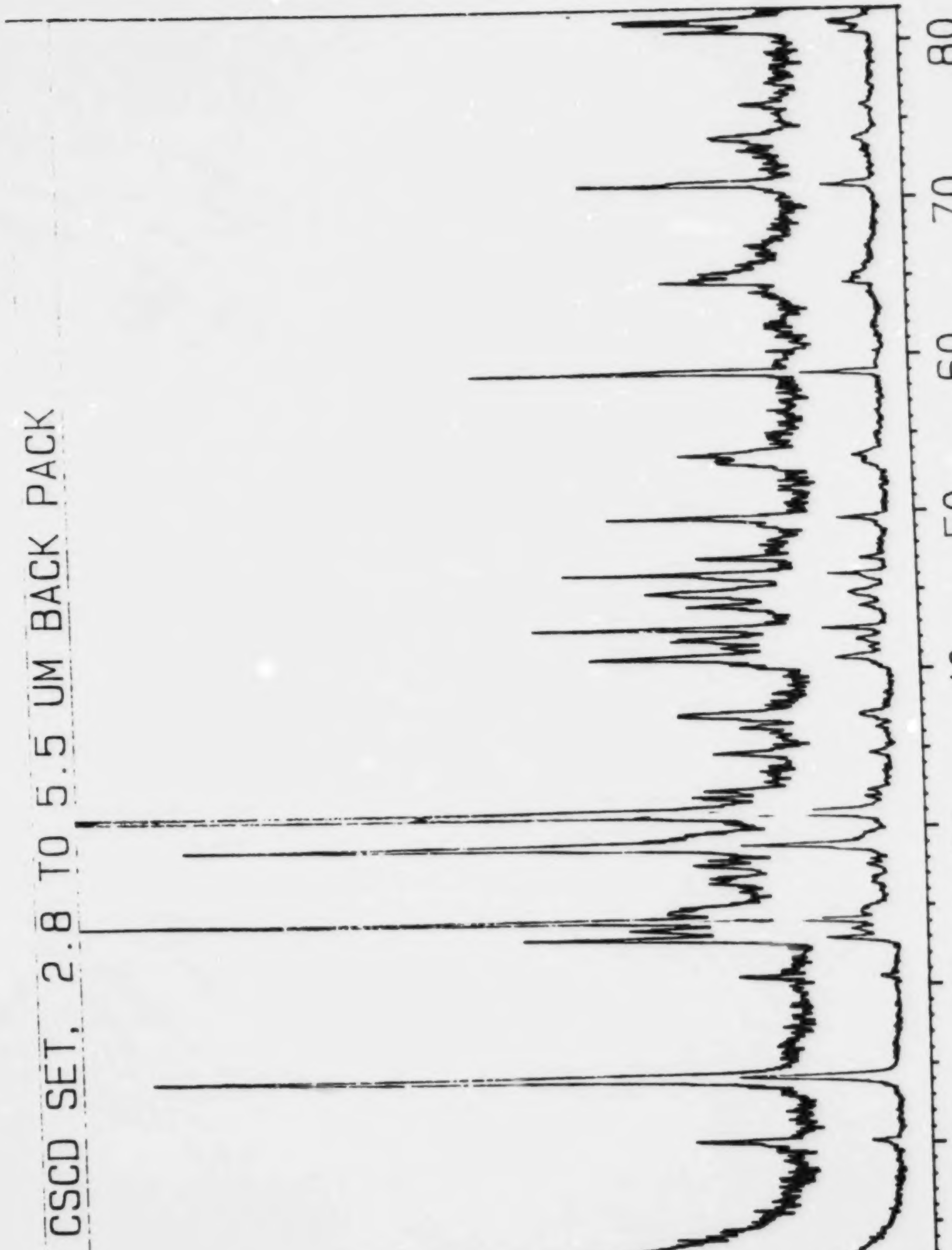
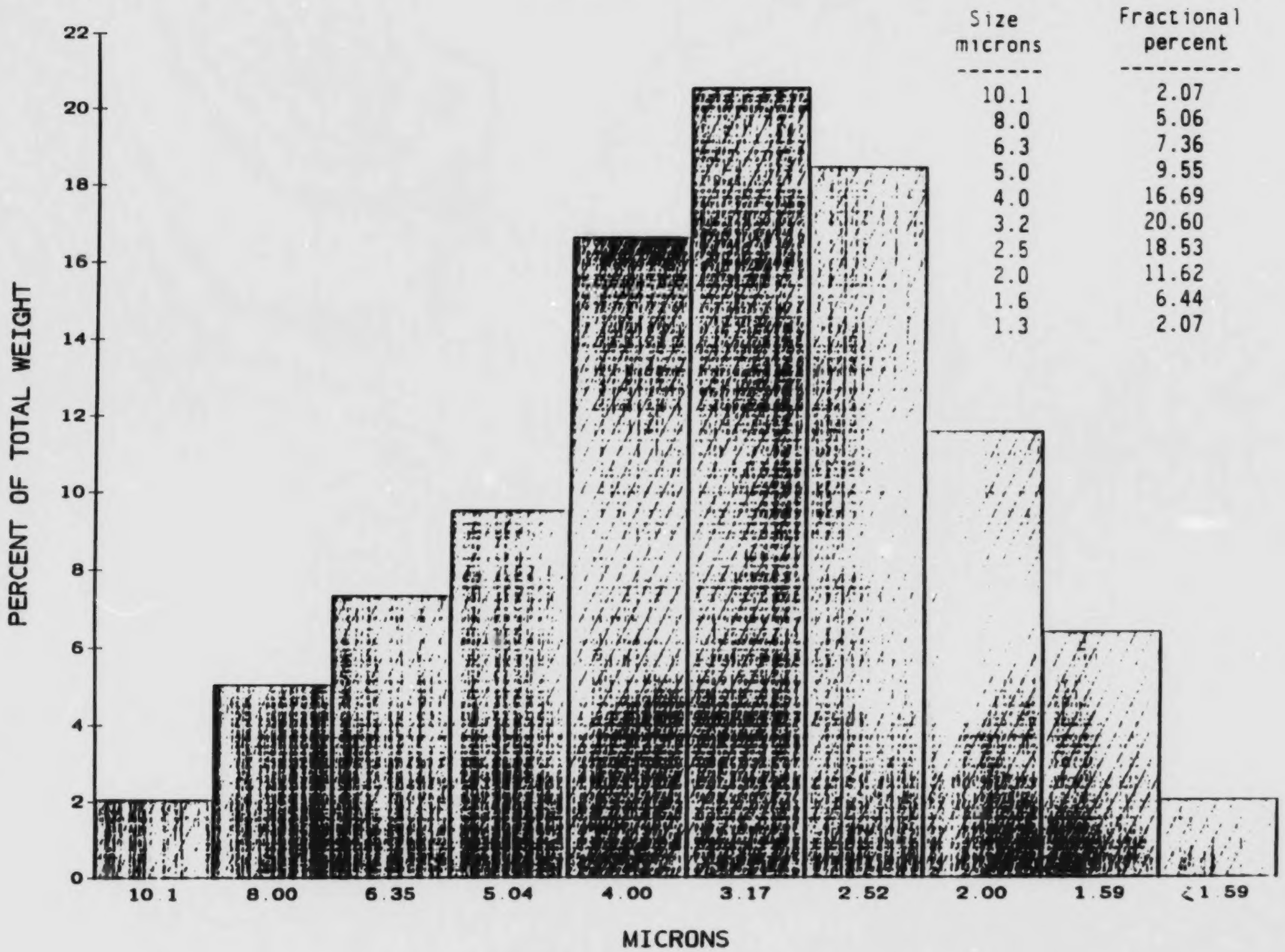


FIGURE 5: Diffractogram of sludge solids fraction 3

PARTICLE SIZE ANALYSIS



Size microns	Fractional percent	Cumulative percent
10.1	2.07	2.07
8.0	5.06	7.13
6.3	7.36	14.50
5.0	9.55	24.05
4.0	16.69	40.74
3.2	20.60	61.33
2.5	18.53	79.86
2.0	11.62	91.48
1.6	6.44	97.93
1.3	2.07	100.00

FIGURE 6: Sludge solids fraction 3

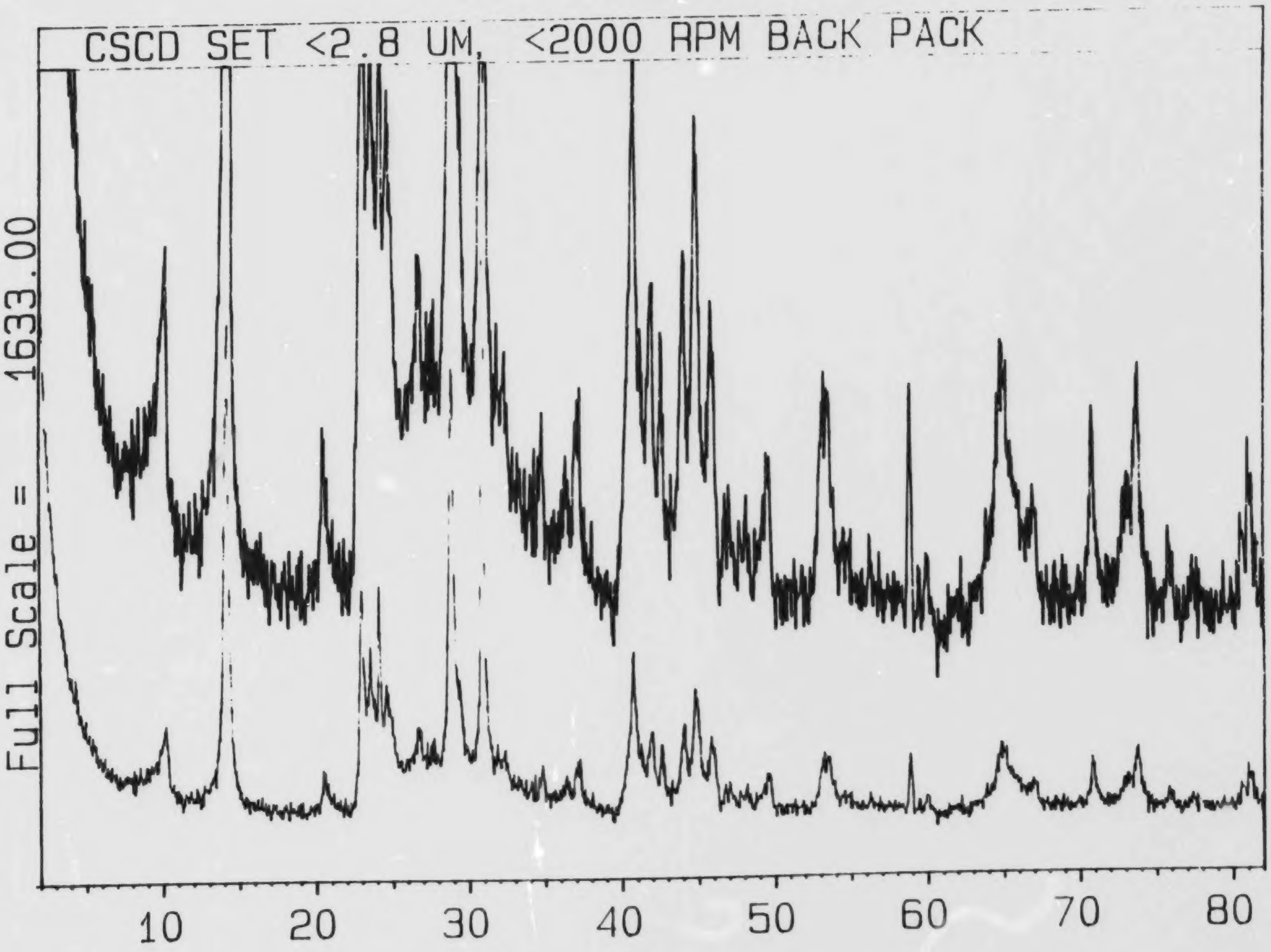
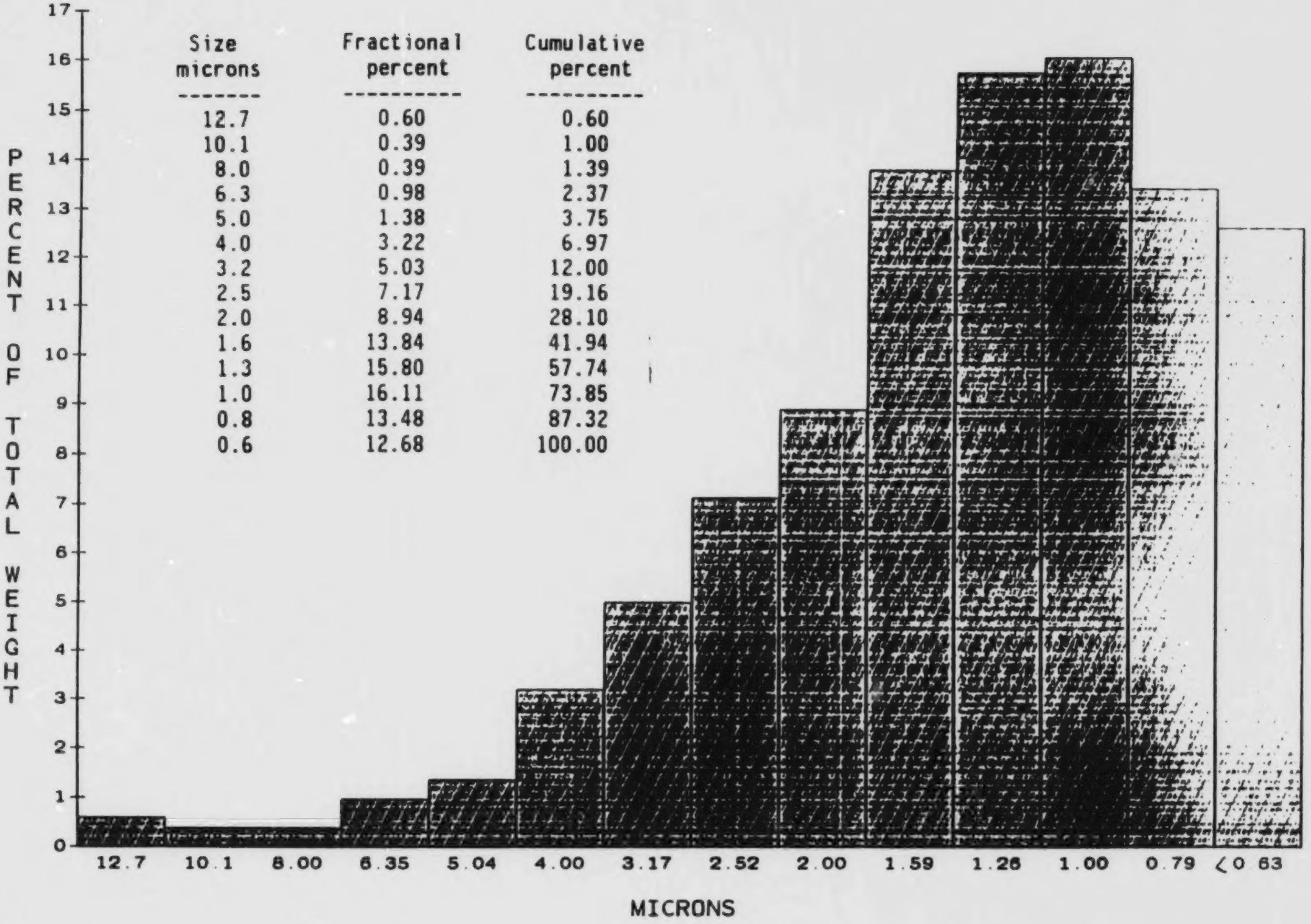


FIGURE 7: Diffractogram of sludge solids fraction 4

PARTICLE SIZE ANALYSIS



Size microns	Fractional percent	Cumulative percent
12.7	0.60	0.60
10.1	0.39	1.00
8.0	0.39	1.39
6.3	0.98	2.37
5.0	1.38	3.75
4.0	3.22	6.97
3.2	5.03	12.00
2.5	7.17	19.16
2.0	8.94	28.10
1.6	13.84	41.94
1.3	15.80	57.74
1.0	16.11	73.85
0.8	13.48	87.32
0.6	12.68	100.00

FIGURE 8: Sludge solids fraction 4

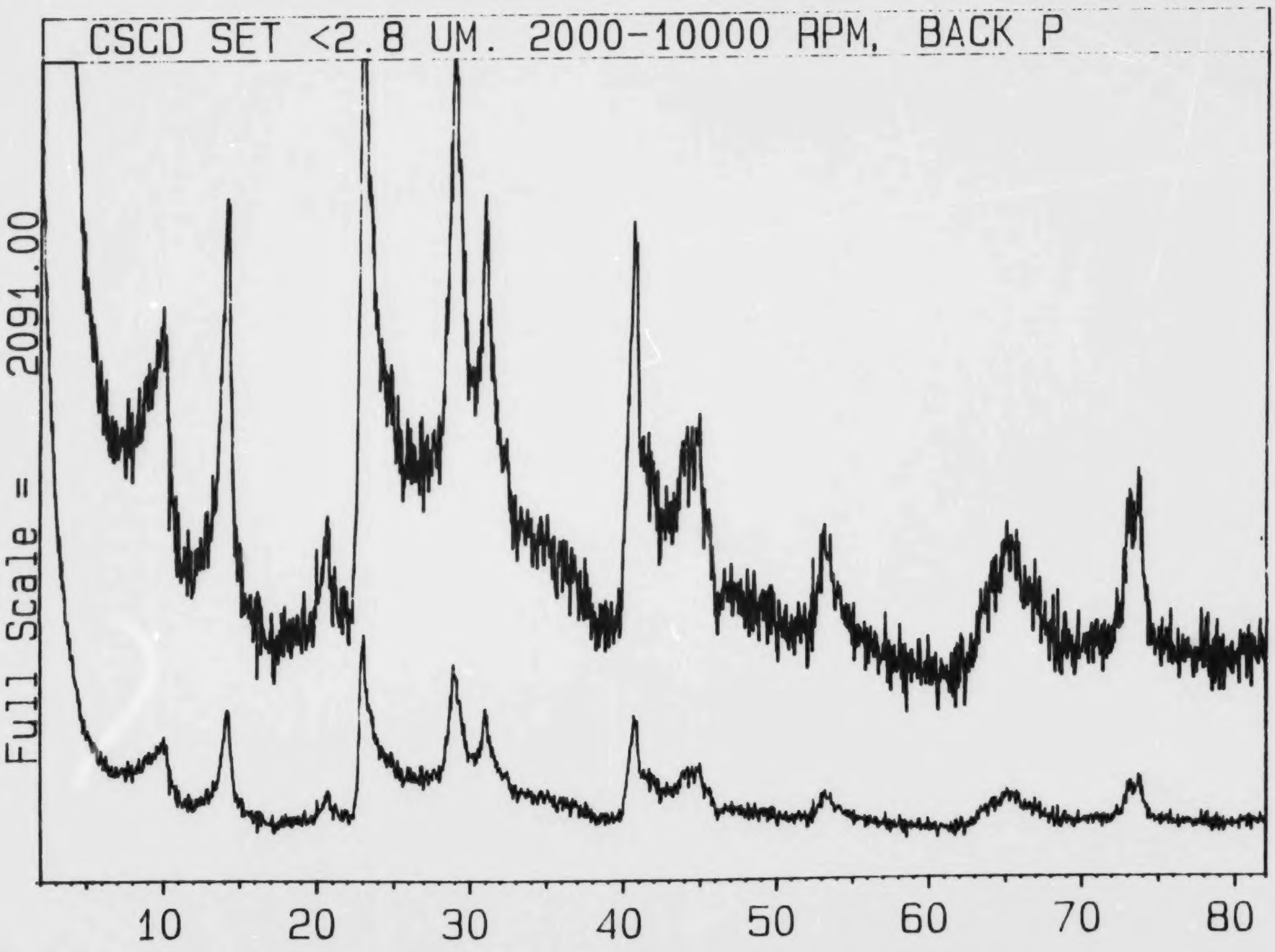
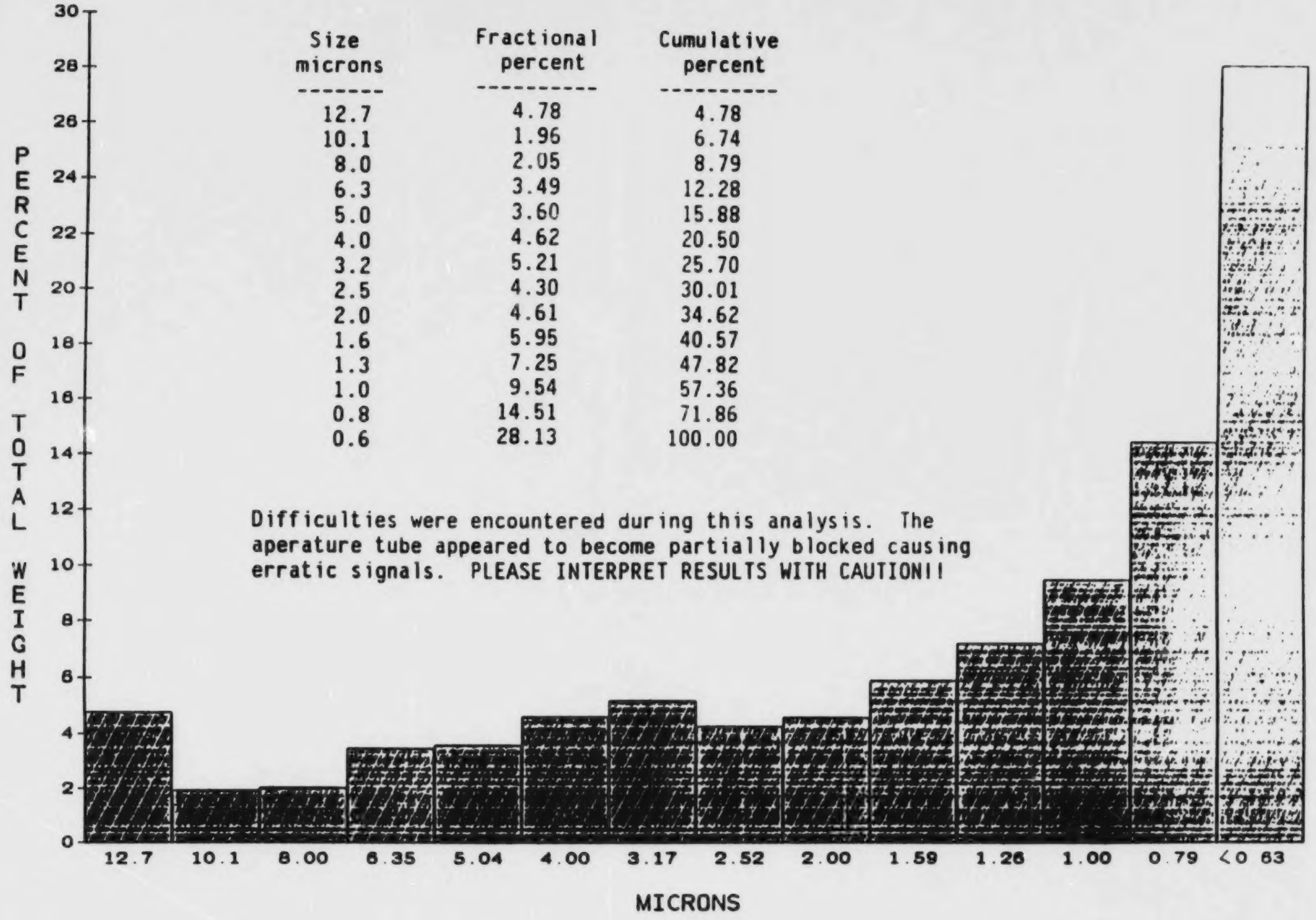


FIGURE 9: Diffractogram of sludge solids fraction 5

PARTICLE SIZE ANALYSIS



Size microns	Fractional percent	Cumulative percent
12.7	4.78	4.78
10.1	1.96	6.74
8.0	2.05	8.79
6.3	3.49	12.28
5.0	3.60	15.88
4.0	4.62	20.50
3.2	5.21	25.70
2.5	4.30	30.01
2.0	4.61	34.62
1.6	5.95	40.57
1.3	7.25	47.82
1.0	9.54	57.36
0.8	14.51	71.86
0.6	28.13	100.00

Difficulties were encountered during this analysis. The aperature tube appeared to become partially blocked causing erratic signals. PLEASE INTERPRET RESULTS WITH CAUTION!!

FIGURE 10: Sludge solids fraction 5

results are shown in Table 4 in units of both mg/L and meq/L. It can be seen that the water basically contains a mixture of dissolved NaCl and $NaHCO_3$ at a pH of 8, and a significant amount of organic carbon.

Rheology

Since sludges are essentially concentrated suspensions of solids, it was decided to study their rheological behavior in order to obtain possible information about their structure. Whole sludge was used and experiments carried out in a Haake RV100 concentric cylinder viscometer with M150B measuring head and MVIII rotor. Homogenized samples were poured into the cup and allowed to sit for a set length of time. The rotor was then introduced and the measurements carried out, all at 25°C.

Two types of results are indicated in Figures 11 and 12. In the first rheogram (Fig. 11) thixotropic behavior, where the viscosity decreases with increase in shear rate and an extrapolation leads to a Bingham yield stress value, is observed (3-5). As the shear rate is decreased for the same sample a hysteresis loop results which depends on the shear history. In the second (Fig. 12) at the early stages of shearing an overshoot stress is observed which appears to depend upon how long the sample sat in the cup prior to introduction of the rotor. The Bingham yield stress value is a measure of the residual interaction potential between the particles. The overshoot stress is associated with an elastic or gel-like structure in a system such as a flocculated suspension.

As mentioned, the magnitude of the overshoot stress depended upon how long the sample sat prior to shearing; results are plotted in Figure 13. Each point corresponds to different subsamples which were initially mixed and allowed to sit for the times indicated on the x-axis before the rotor was introduced and shearing begun. The results show a pronounced peak at about 12 h, which may indicate the time for the system to attain a well-defined structure. It is not known why the overshoot decreases at times greater than 12 h. The rheograms corrsponding to all points in Figure 13 are given in Appendix 1, with their respective times indicated in min or h.

For a number of samples, after the initial measurements the rotor was kept in the sample for the same length of time as before the initial introduction of the rotor, after which a second measurement was carried out. The results are shown in Figure 14, in which the x-axis indicates the time since the first shearing of the sample (ie. the time the sample sat in the viscometer with the rotor immersed). The corresponding rheograms are all shown in Appendix 2. The data from Figure 13 is also shown for comparison. In most cases the overshoot stress was higher than when the rotor was first immersed in the sludge, and interestingly the peak overshoot also occurred at 12 h. The higher overshoot stress could indicate two things. First, measurement directly following rotor immersion may break up the sludge gel structure. Second, with the rotor immersed bitumen may stick between the walls of the cup and the rotor and have an effect.

In summary, this brief rheology study indicates that whole sludge is thixotropic and has a definite structure which is somewhat dependent upon the time since it was vigorously sheared.

TABLE 4: **Water Chemistry of Sludge Water**

	mg/L	meq/L
Na	455.0	19.8
K	9.0	0.2
Ca	6.3	0.3
Mg	4.3	0.4
B	1.9	0.2
Fe	0.2	-
Cl	116.0	3.3
SO_4	2.4	0.1
HCO_3	1025.0	16.8
CO_3	20.0	0.7
TIC	209.0	
TOC	92.0	
pH	8.18	

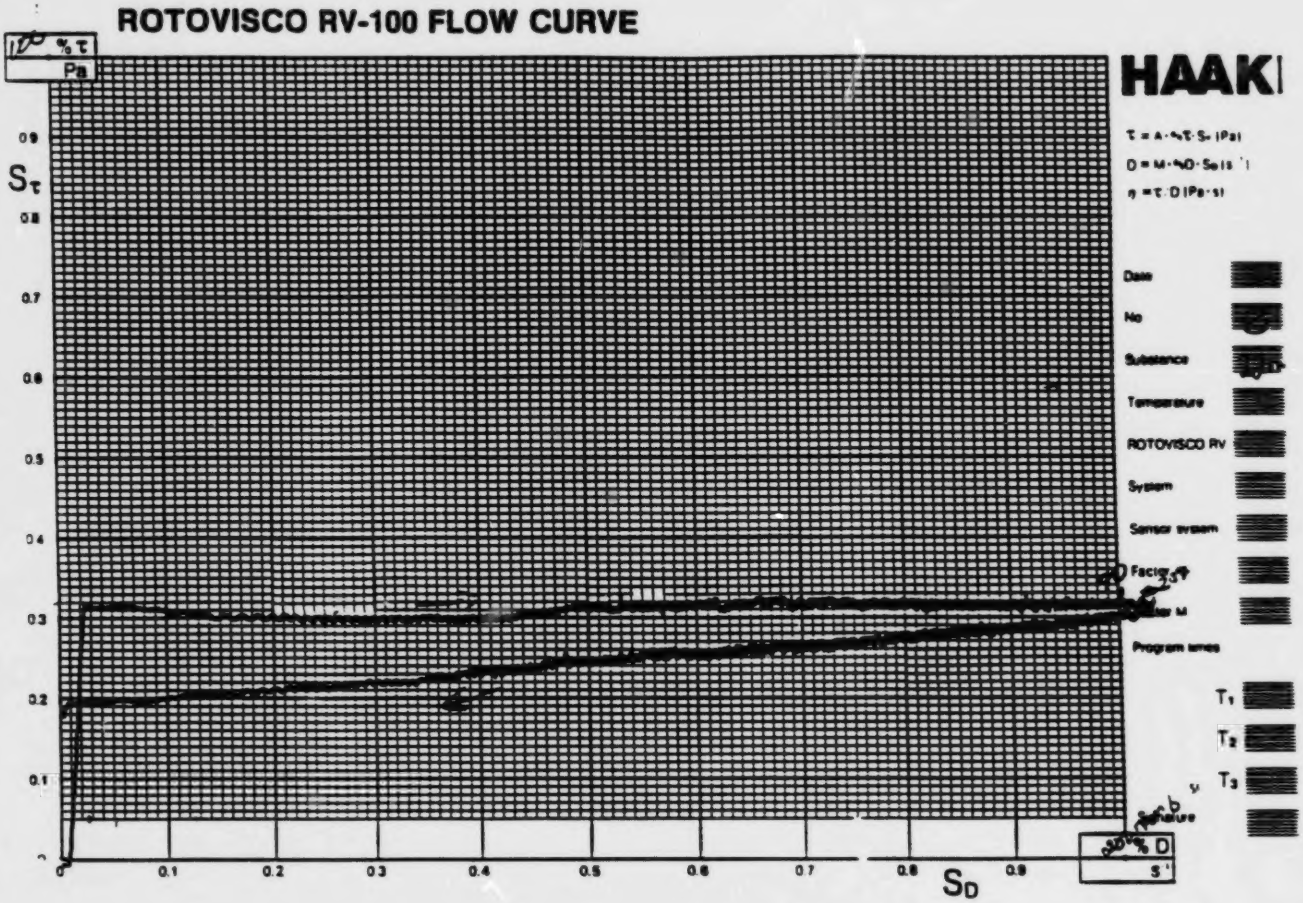


FIGURE 11: Rheogram of the sludge sample which sat in the cylinder for 22 minutes before shearing.

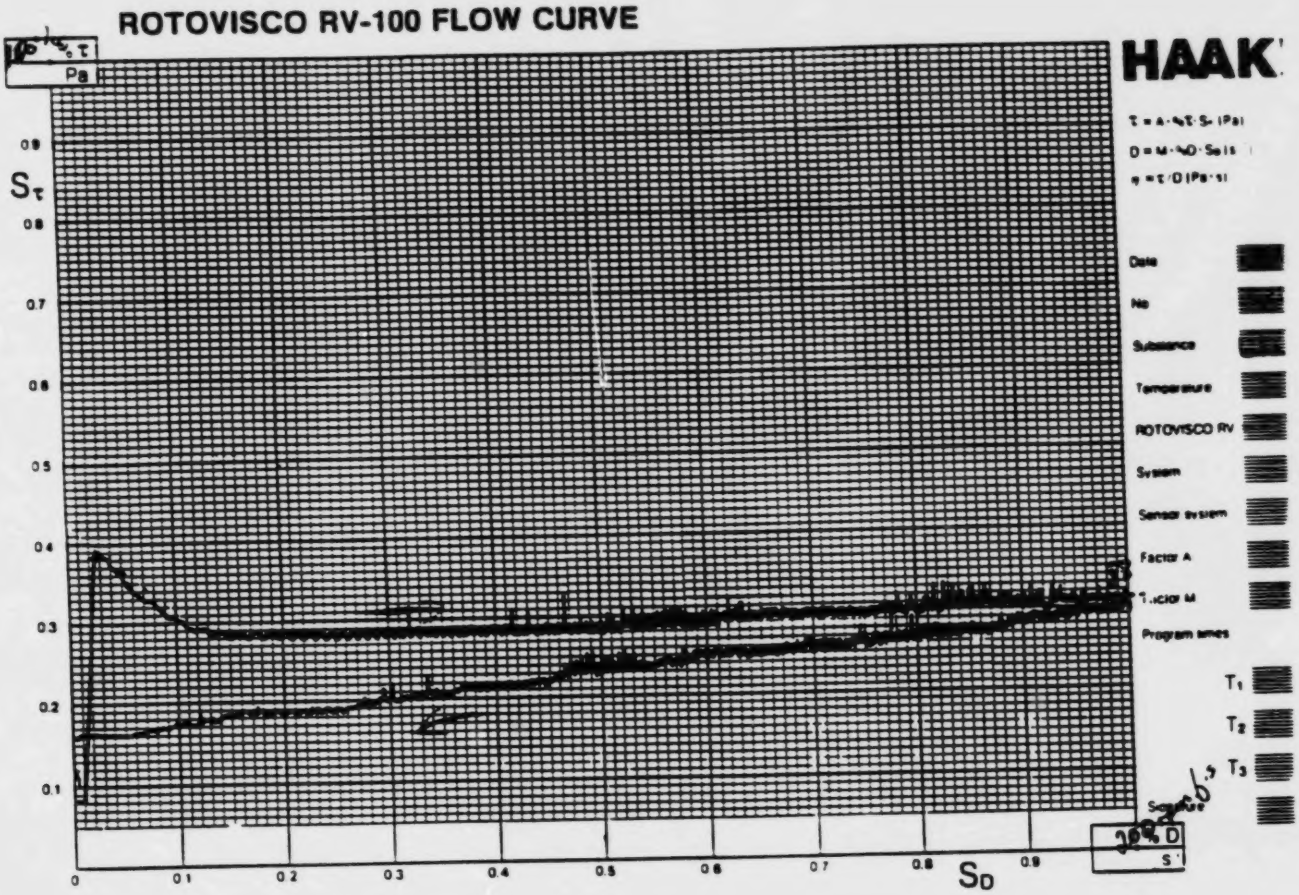


FIGURE 12: Rheogram of the sludge sample which sat in the cylinder for 6 hours before shearing. Notice the pronounced overshoot stress at the early stages of shearing.

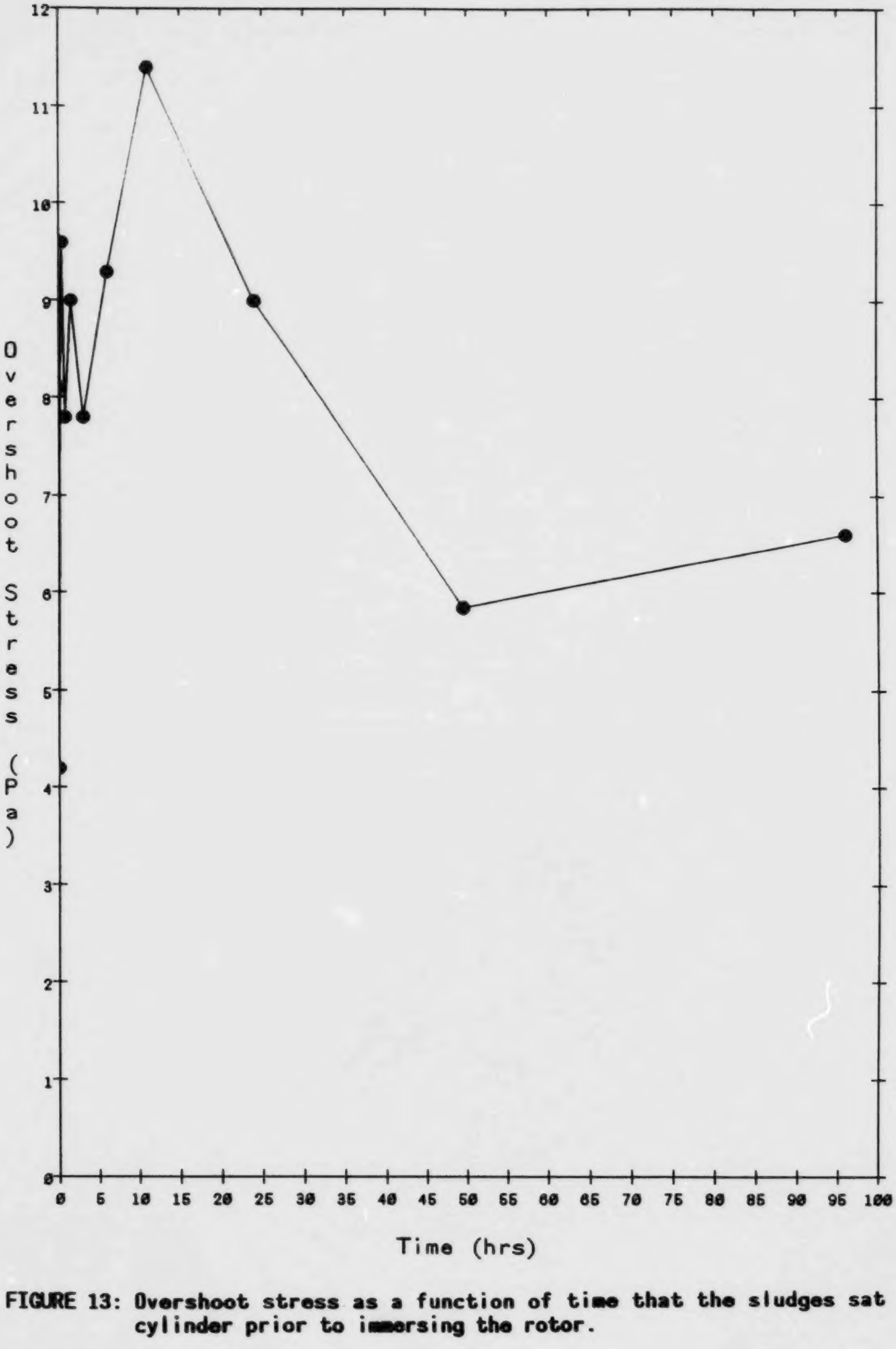


FIGURE 13: Overshoot stress as a function of time that the sludges sat in the cylinder prior to immersing the rotor.

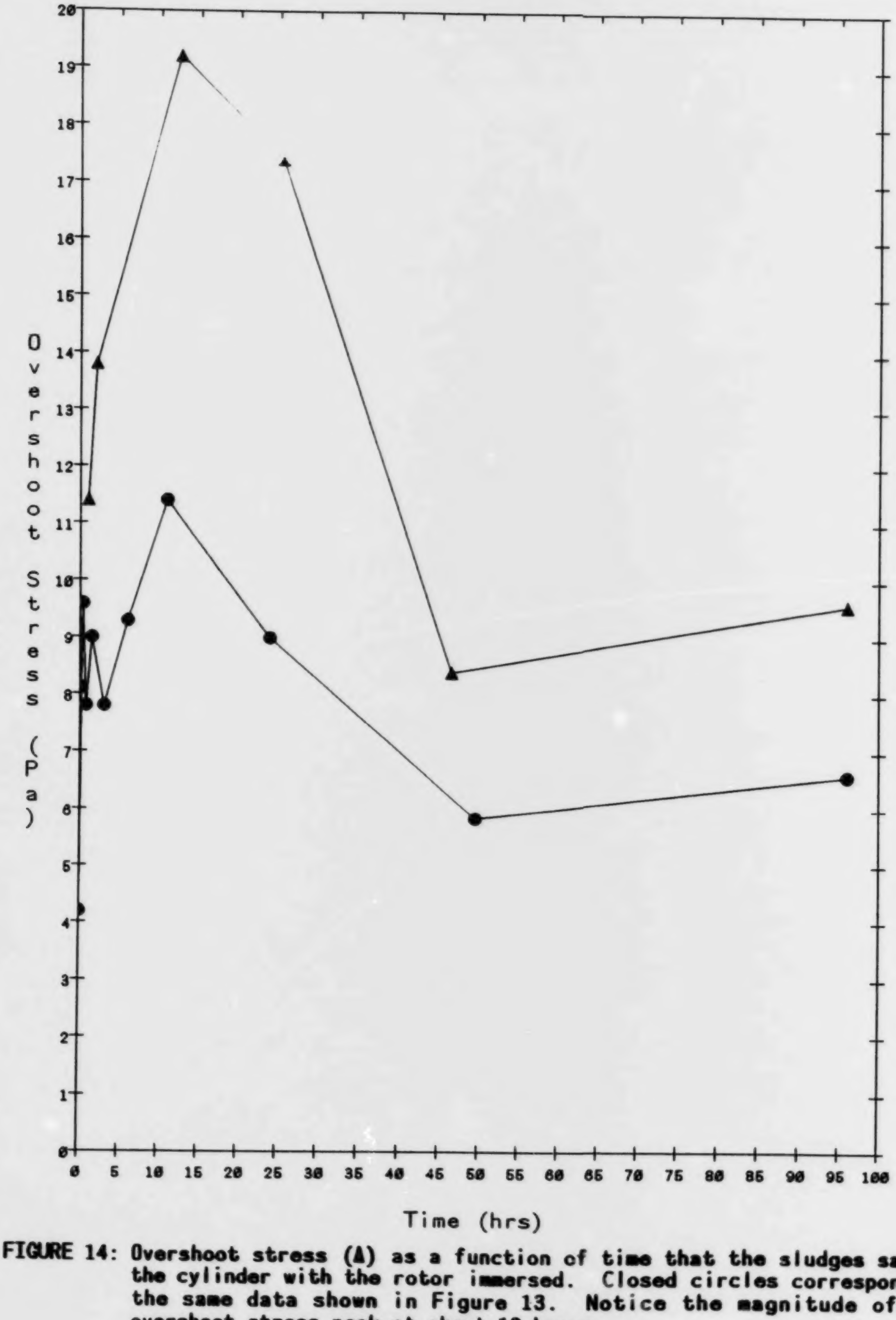


FIGURE 14: Overshoot stress (▲) as a function of time that the sludges sat in the cylinder with the rotor immersed. Closed circles correspond to the same data shown in Figure 13. Notice the magnitude of the overshoot stress peak at about 12 hours.

EFFECTS OF NACL ON SLUDGE PROPERTIES

Rheology

The amount of NaCl in the original sludge water as seen from Table 4 is high enough to result in some flocculation as already indicated by the measured overshoot stress. Therefore, it was decided to study the effects on the rheology of higher levels of salts, and to see if there were any correlations with the settling properties of the sludge.

The appropriate amounts of NaCl were weighed into a bottle, sludge added and the mixture shaken. About 70 mL of the mixture was poured into the viscometer cup and allowed to set for 1.5 h, which from the previous experiments, was within the time for which the overshoot stress was approximately constant. After the cup was attached to the rotor, the sample was allowed to "recover" for five min. prior to running. The Haake RV100 with M150B measuring head and MVIII rotor was used. The shear rate was programmed from 0 to 88 s^{-1} in 2 min. and back to 0 also in 2 min.

The rheology curve for the whole sludge with no added NaCl (0.02 M in the original sludge water) is shown in Figure 15. The shear rate range for this one case was less than the range for all the others. The remainder of the curves for various amounts of salt added are shown in Figures 16 to 21. Most of these curves exhibit pseudoplastic behavior, but can be fitted to a Bingham model using an extrapolated yield stress value (4). The parameters which can be calculated assuming this model are indicated in Figure 15.

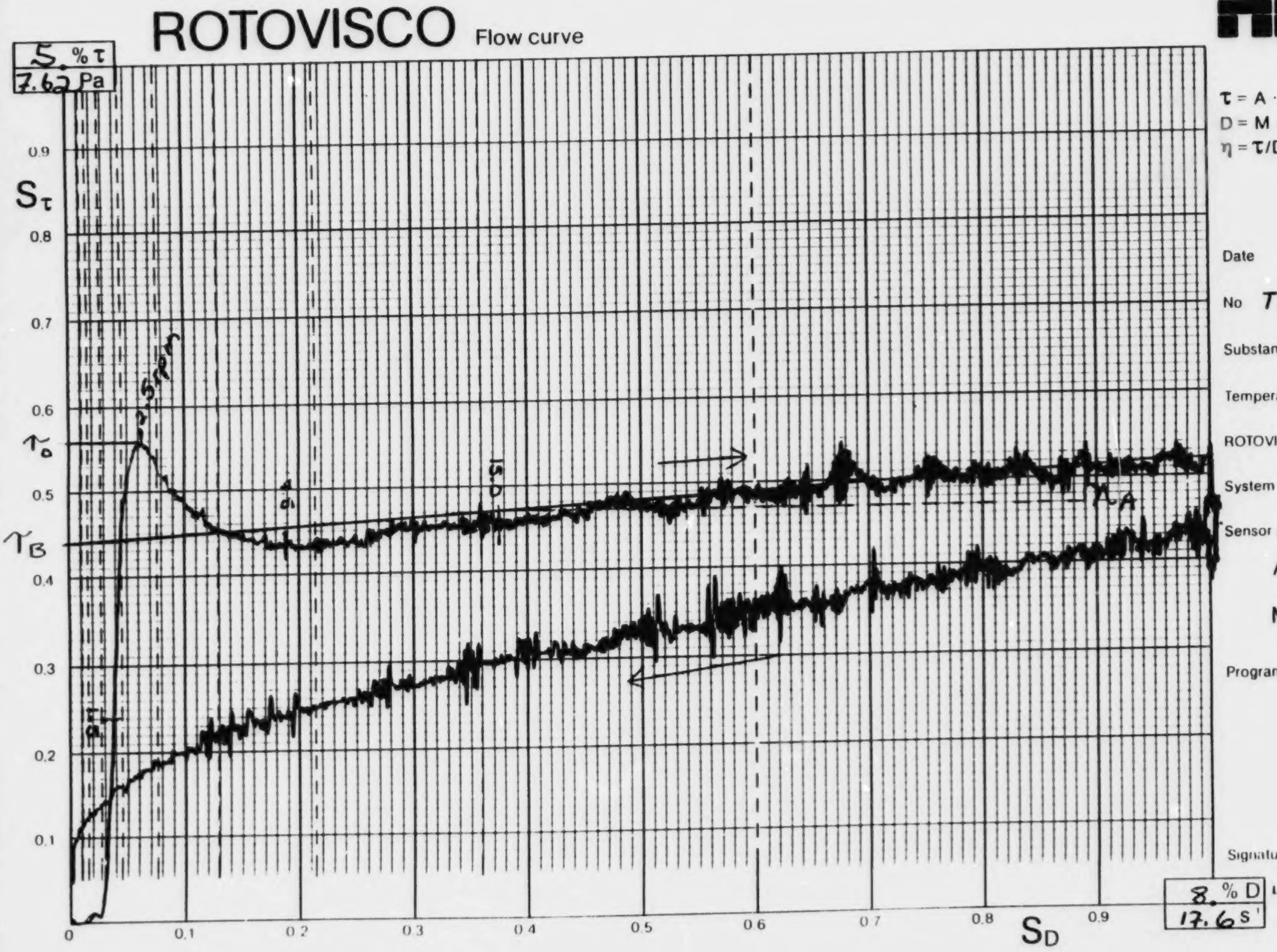
As already indicated, the Bingham yield stress value, τ_B, is a measure of the residual interaction potential between particles. It is obtained by extrapolation of the linear portion of the curve to the y-axis. The rapid increase in the stress at low shear rates is called the overshoot stress, τ_O, and is associated with an elastic structure in a system such as a flocculated suspension. The slope of the linear portion of the curve is the apparent viscosity, η_A. This occurs above the critical shear rate, γ_C.

A definite overshoot stress is observed in all curves up to 0.12 M NaCl, but becomes much less pronounced, if not negligible, beyond this concentration. It could probably be considered negligible since its value would be less than that of the yield stress at these higher concentrations. The calculated yield stress, overshoot and apparent viscosity for all concentrations are listed in Table 5. It can be seen that the yield stress increases continuously as the salt concentration increases, indicating that the residual interaction potential between solid particles is continuing to increase. The overshoot stress increases up to 0.08 M and then becomes negligible as indicated previously, indicating that the elastic structure, probably due to the flocculation, increases up to this point after which its effect subsides. This could be since the double layer thickness has been compressed by the salt to its minimum value. Finally, the

TABLE 5: Parameters Calculated from the Rheological Curves of Whole Sludge Containing Varying Amounts of NaCl

NaCl (M)	Yield Stress τ_B (Pa)	Overshoot τ_o (Pa)	Apparent Viscosity η_A (mPa•s)
0.02	3.35	4.27	30.3
0.04	4.57	8.87	27.7
0.06	7.32	12.9	24.3
0.08	7.92	13.9	24.3
0.12	11.9	13.3	27.7
0.22	16.8	-	27.7
0.32	22.3	-	21.0
			26.6±2.4

$$\tau = \eta_A \gamma + \tau_B$$



Sat 5 min with rotor & run

$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]

$D = M \cdot \%D \cdot S_D$ [s⁻¹]

$\eta = \tau / D$ [Pa · s]

Date June 15/89

No T∅ Run #3

Substance #7-1.5 hr.

Temperature 25.2.

ROTOVISCO RV 100

System M150B

Sensor system MV III

A 1524

M 0.44

Program time

t_1 0

t_2 0.4

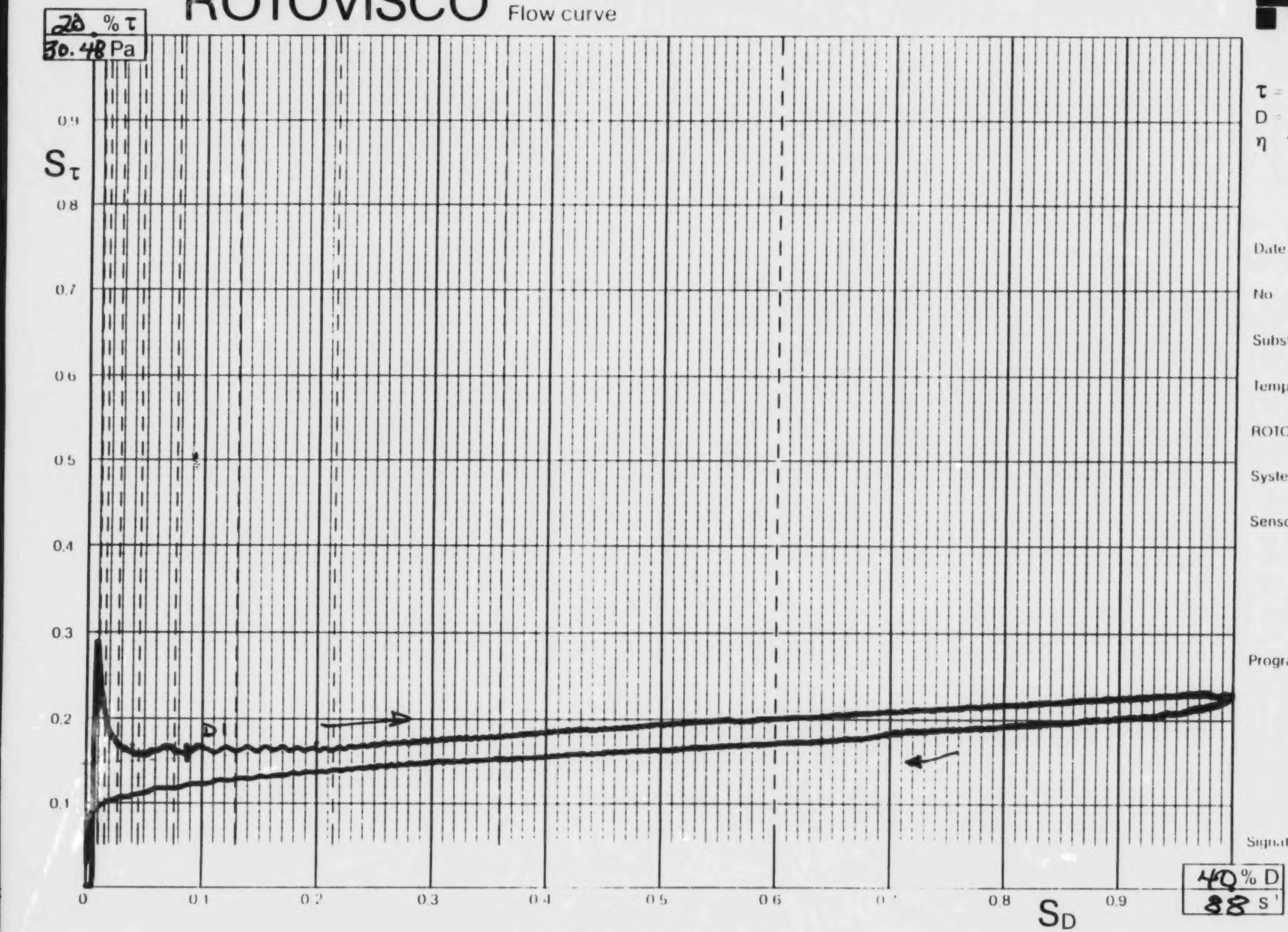
t_3 3.2

Signature

FIGURE 15: Original sludge rheogram
0.02 M NaCl

ROTOVISCO Flow curve

HBI



$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]
$D = M \cdot \%D \cdot S_D$ [s⁻¹]
$\eta = \tau / D$ [Pa·s]

Date	June 29/89
No	NaCl 2 (Rer
Substance	SL + .02 NaCl.
Temperature	24.9
ROTOVISCO RV	100
System	M150B
Sensor system	MVIII
A	1534
M	0.44

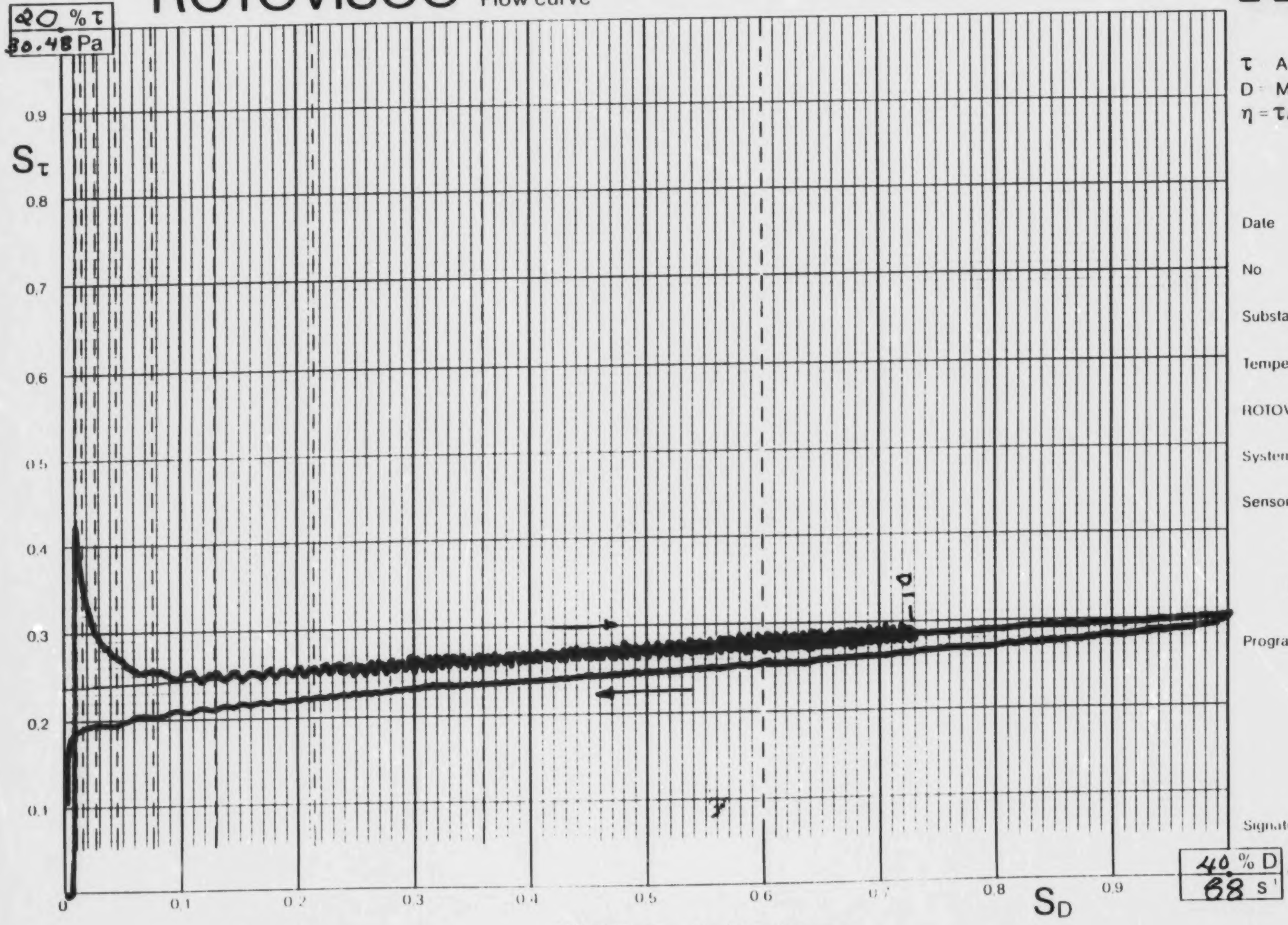
Program time
t_1 0
t_2 2 min
t_3 0

Signature KEP

FIGURE 16: Sludge rheogram
0.04 M NaCl

HBI

ROTOVISCO Flow curve

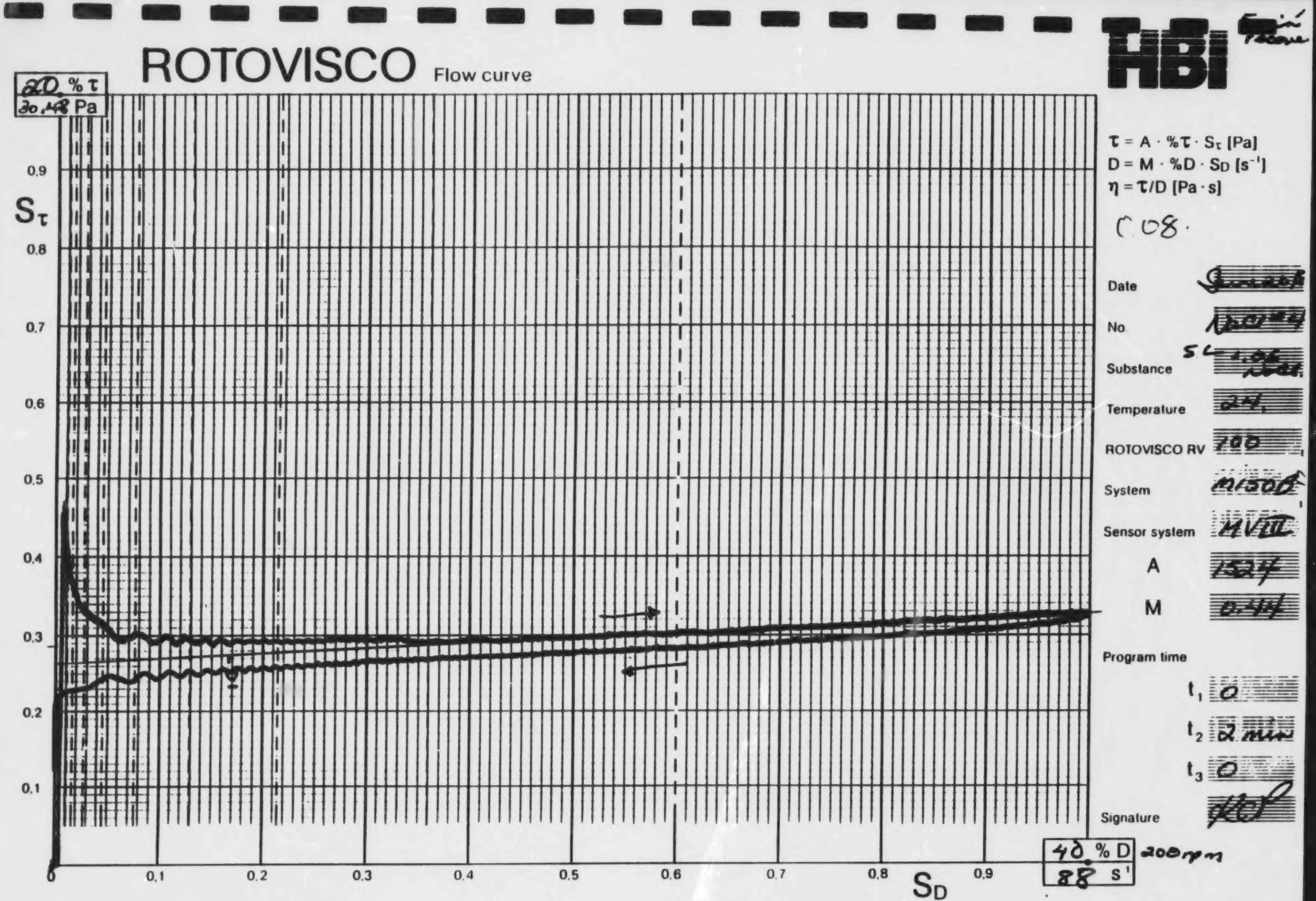


$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]
$D = M \cdot \%D \cdot S_D$ [s^{-1}]
$\eta = \tau / D$ [Pa · s]

Date	June 26/89
No	NaCl # 3
Substance	SL + 0.4M NaCl
Temperature	24.6
ROTOVISCO RV	100
System	M150B
Sensor system	MVIII
A	1524
M	0.44
Program time	
t_1	6
t_2	2 min.
t_3	0
Signature	KCP

200 rpm

FIGURE 17: Sludge rheogram
0.06 M NaCl

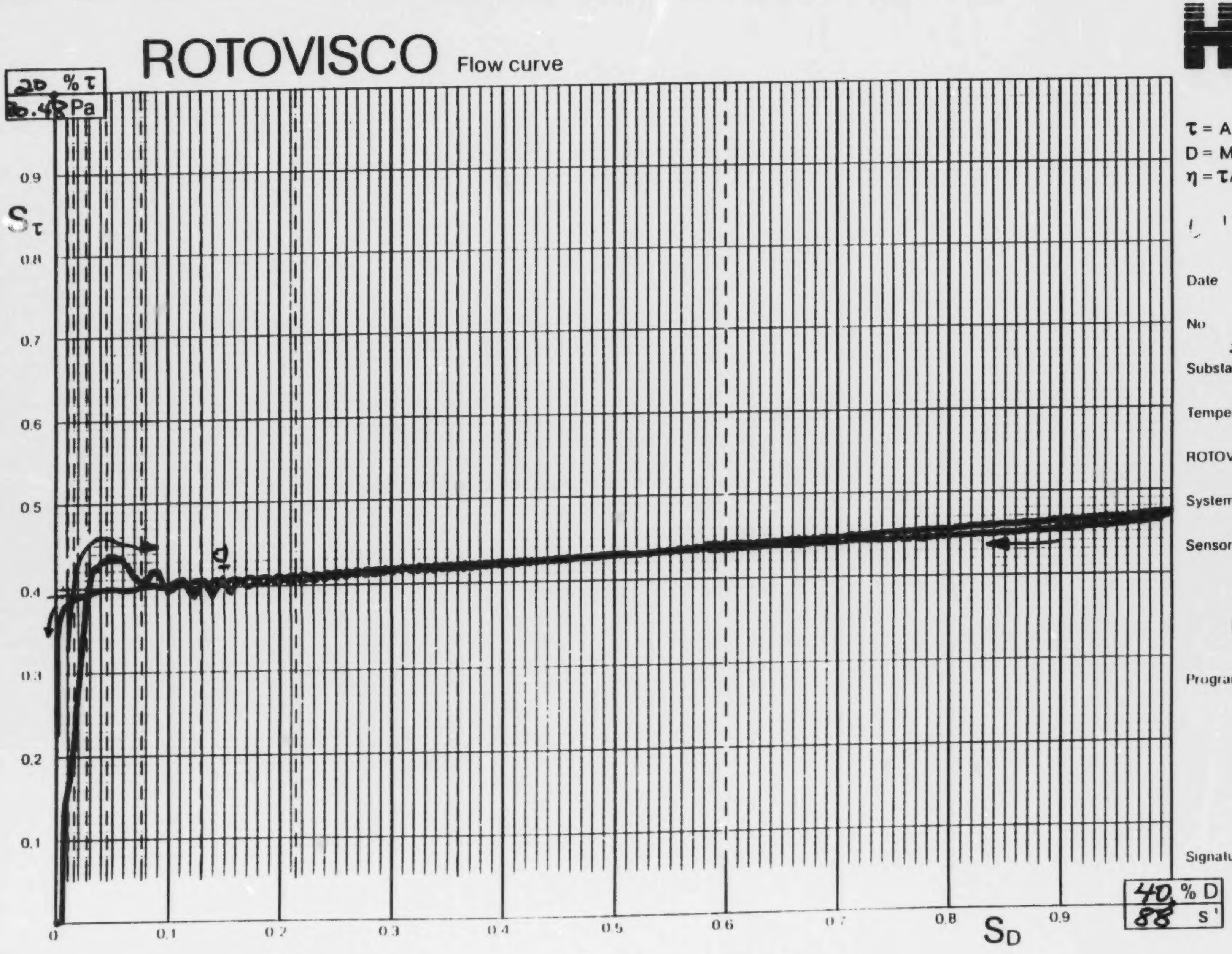


τ = A · %τ · Sτ [Pa]
D = M · %D · SD [s⁻¹]
η = τ/D [Pa · s]

0.08.

Date [illegible]
No [illegible]
Substance SL [illegible]
Temperature 24
ROTOVISCO RV 100
System M150B
Sensor system MVIII
A 1524
M 0.44
Program time
t₁ 0
t₂ 2 min
t₃ 0
Signature

FIGURE 18: Sludge rheogram
0.08 M NaCl



$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]
$D = M \cdot \%D \cdot S_D$ [s^{-1}]
$\eta = \tau / D$ [Pa · s]

1, 12

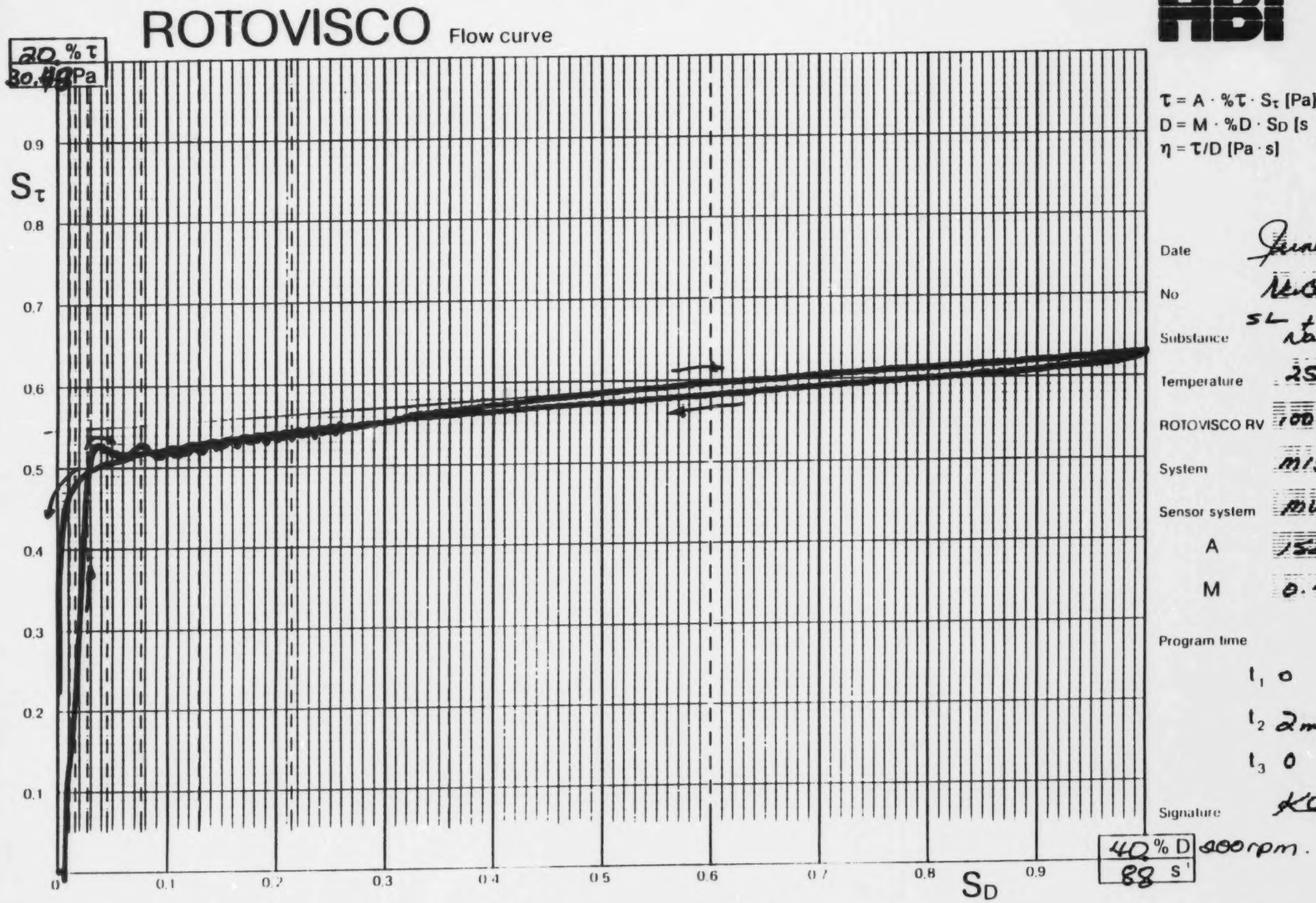
Date	June 29 11
No	NaCl #5 R1
Substance	SL + .1 NaCl.
Temperature	24.9
ROTOVISCO RV	100
System	M150B
Sensor system	MVIII
A	1524
M	0.44

Program time

t_1	0
t_2	2min
t_3	0

Signature KCF

FIGURE 19: Sludge rheogram
0.12 M NaCl



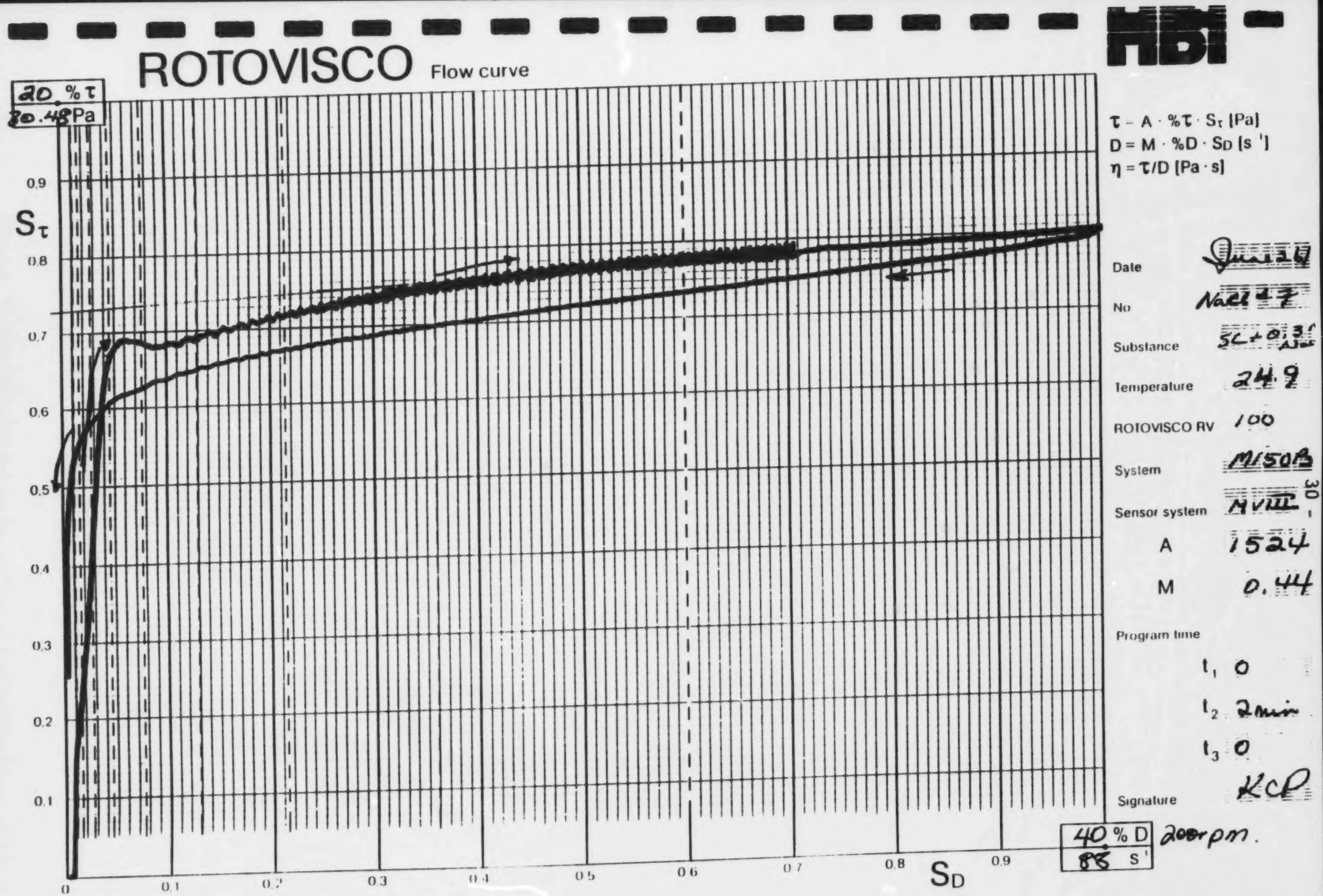
$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]
$D = M \cdot \%D \cdot S_D$ [s^{-1}]
$\eta = \tau / D$ [Pa · s]

Date June 26/8
No [illegible]
Substance SL 1:21 NaCl.
Temperature 25.0
ROTOVISCO RV 100
System M150B
Sensor system MVIII
A 15.24
M 0.44

Program time
t_1 0
t_2 2min
t_3 0

Signature KOP

FIGURE 20: Sludge rheogram
0.22 M NaCl



$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]
$D = M \cdot \%D \cdot S_D$ [s⁻¹]
$\eta = \tau / D$ [Pa · s]

Date June 24
No NaCl 27
Substance SC+0.32 NaCl
Temperature 24.9
ROTOVISCO RV 100
System M150B
Sensor system MVIII 30
A 1524
M 0.44
Program time
t_1 0
t_2 2min
t_3 0
Signature KCP

FIGURE 21: Sludge rheogram
0.32 M NaCl

apparent viscosity does not significantly change over this concentration range; its mean and standard deviation is 26.6±2.4 mPa-s. This indicates that at any of the salt concentrations studied, once the original structural forces have been overcome, the viscosity is more or less constant and probably due mainly to hydrodynamic effects. The trends in yield stress and overshoot stress are also depicted in Figure 22.

Electrokinetic Data

As noted in Figure 23 the electrokinetic data using the Electrokinetic Sonic Analysis (ESA) indicate significant reduction in the absolute value of the mobility as the concentration of NaCl reaches high values. This may result from a significant reduction in the double layer thickness. In order to make these measurements, the original sludge in these experiments was diluted by a factor of about eight using sludge water, to yield a sludge solids concentration of 1.5 vol%. The large discontinuity around the zero point of charge, as seen in Figure 23, may be a result of destabilization of the sludge which is indicated by the centrifugation and settling experiments to be discussed.

Centrifugation Tests

In order to correlate the effect of NaCl to sludge stability, a simple centrifuge test was used. This test was not meant to be an absolute measure of sludge volume reduction, but just a rapid method to indicate the trends. Samples of the same solids concentration as those used for the electrokinetic experiments were prepared in 100 mL glass conical tubes filled to the 100 mL mark. They were centrifuged in a bench top centrifuge for a total of 40 min., and the interface between clear water and sludge monitored every 10 min. The results are shown in Figure 24. The plot indicates that by a concentration of 0.12 M the sludge is sufficiently destabilized such that centrifugation for only 10 min. produces a minimum volume. Beyond this concentration no further reduction in sludge volume was observed. The ESA data in Figure 23 also showed a substantial reduction in the absolute value of the mobility by this salt concentration.

The final solids concentration for all salt contents under these centrifuge conditions, is only 10 vol% (an increase from 1.5 vol%) which is still not a large volume reduction. This corresponds to an increase from 3.5 wt% to 22.4 wt%.

Settling Tests

Settling data at these same concentrations were also obtained over a relatively short time period in order to indicate the general trends. The results are shown in Figure 25. The trend is similar to the centrifuge data with the 0.12 M and higher concentrations producing the lowest sludge volumes.

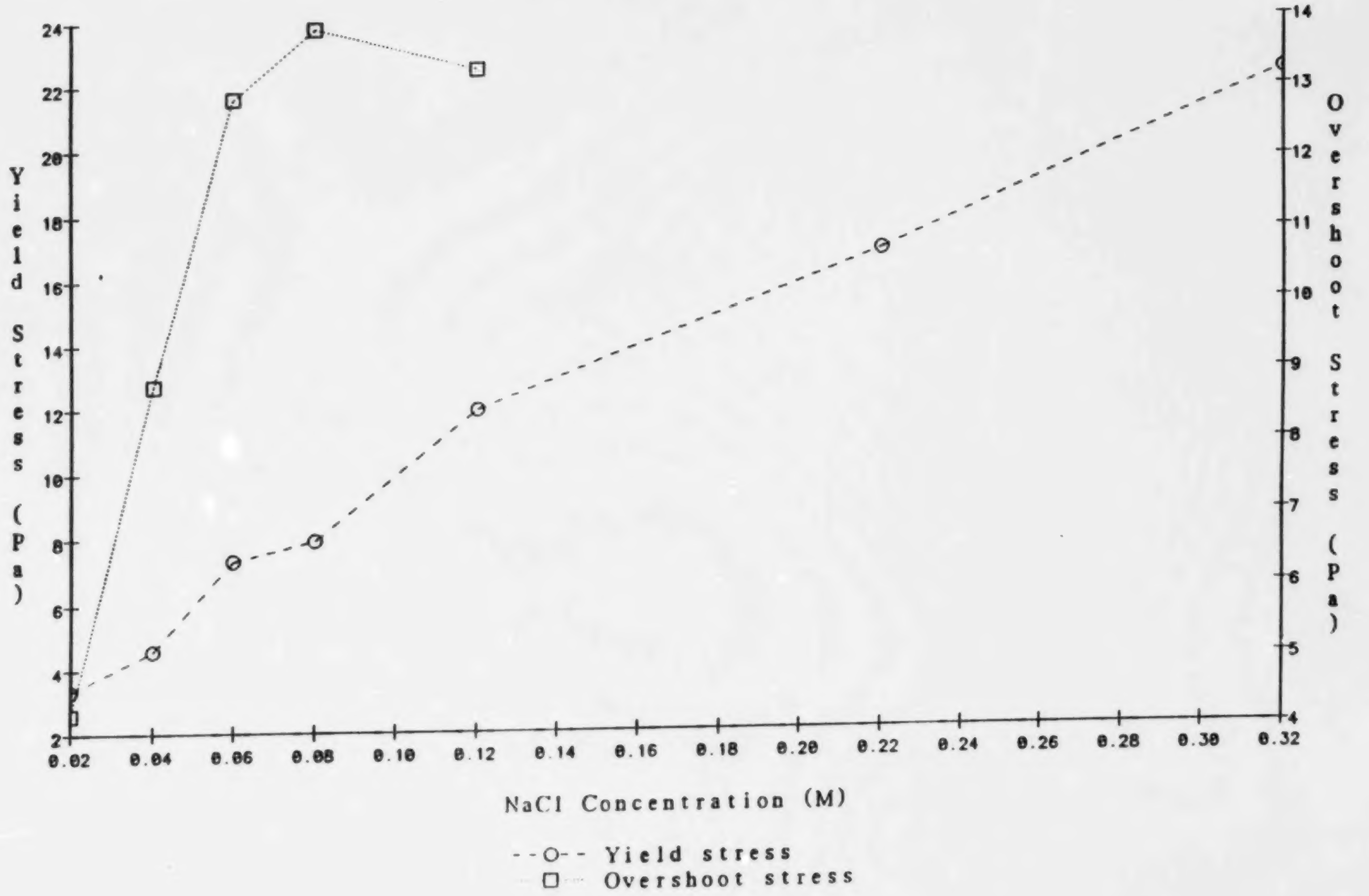


FIGURE 22: Effect of NaCl on Sludge Rheology

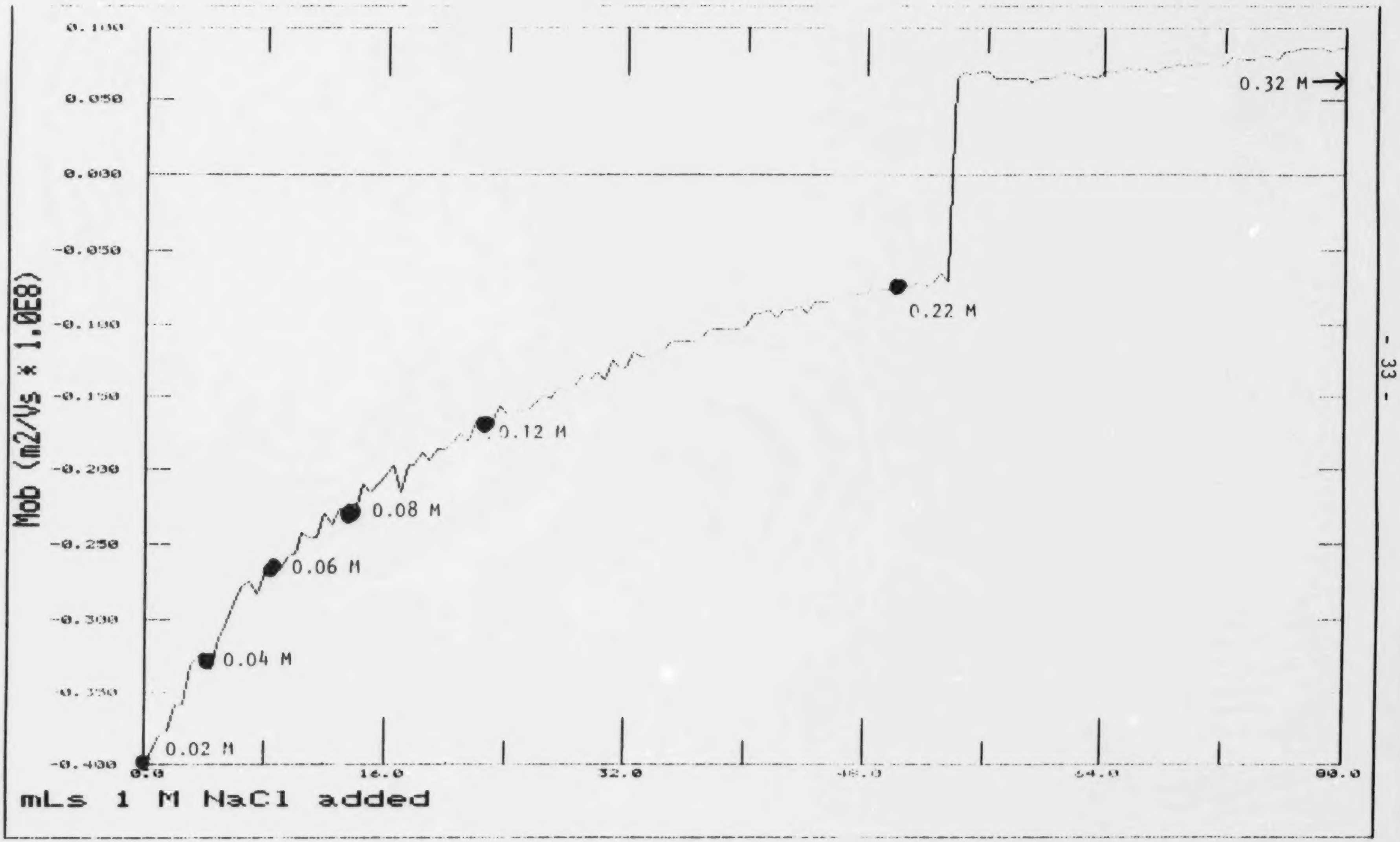


FIGURE 23: Effect of NaCl on Mobility by ESA

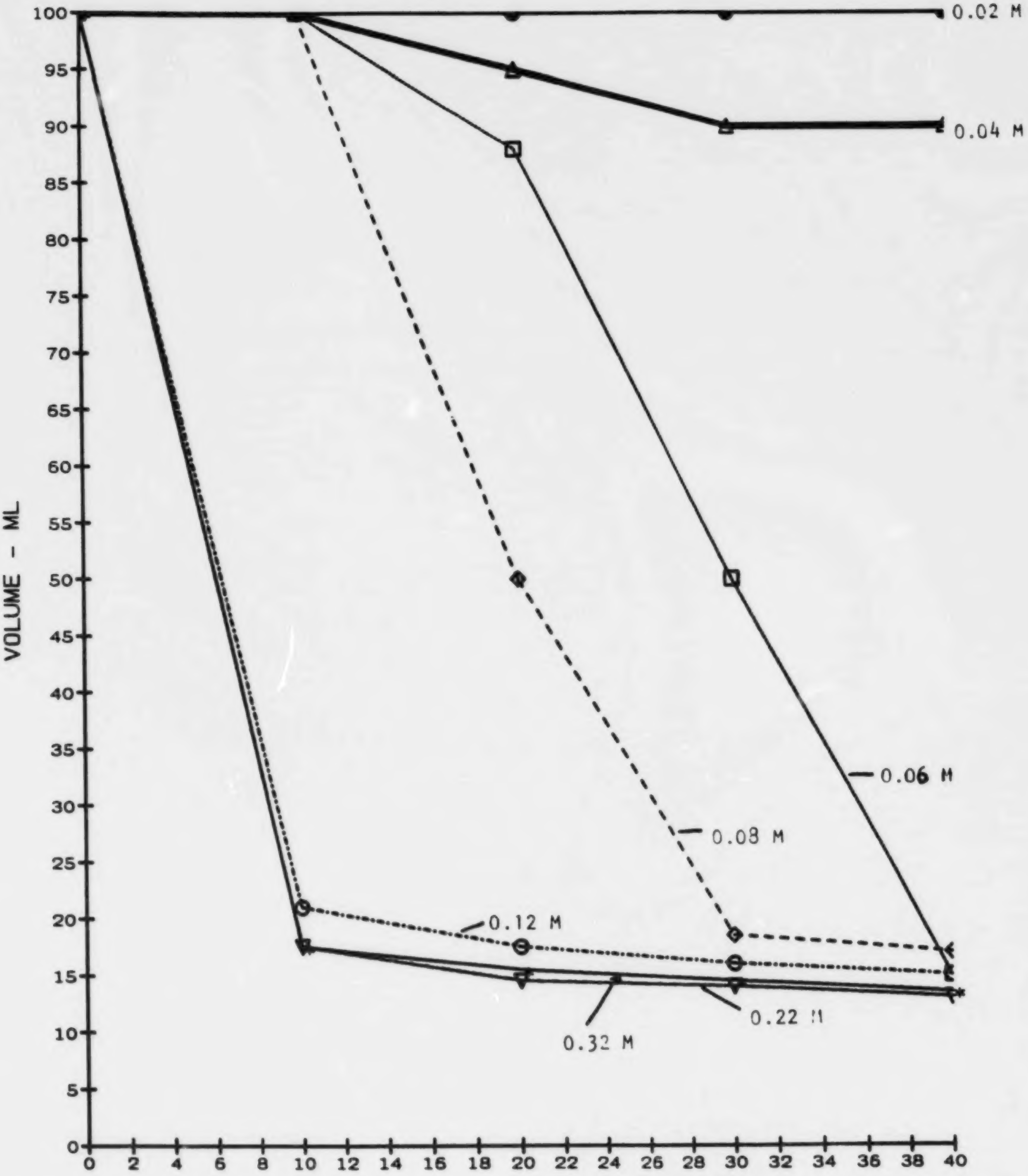


FIGURE 24: Effect of NaCl on Centrifuge Test

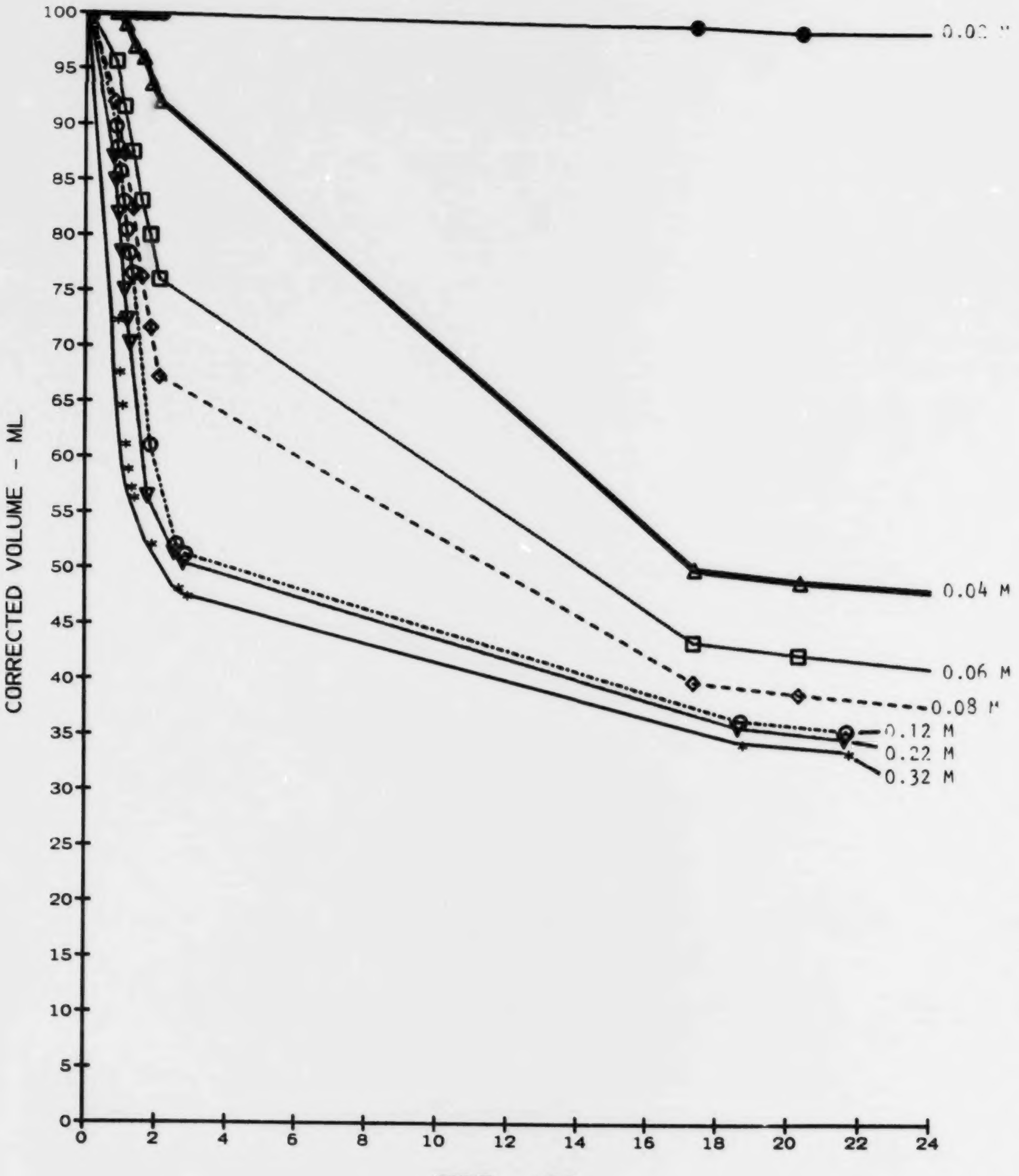


FIGURE 25: Effect of NaCl on Settling

Conclusions

The rheology of the original sludge with its accompanying overshoot stress indicates a flocculated system with a gel-like structure. Addition of NaCl beyond the initial level of 0.02 M appears to strengthen the structure as indicated by the overshoot stress, up to a salt concentration of about 0.12 M. This observation is consistent with the centrifuge and settling data which show the largest change in sludge instability by this concentration. The electrokinetic results also indicate the greatest rate of reduction in mobility by this concentration.

Beyond this salt concentration the overshoot stress drops off but the yield stress continues to increase, indicating an increase in the residual interaction potential between the particles. The apparent viscosity remains relatively constant over the entire concentration, indicating that once the original structural forces have been overcome, the viscosity is due mainly to hydrodynamic effects.

ORGANIC EXTRACTION AND CHARACTERIZATION

Extraction

The loosely bound organic material (presumably bitumen) in the sludge was removed using a number of solvents. It was thought that this material could have an effect on sludge stability, and therefore should be characterized. Sludge was centrifuged at 10,000 rpm for one hour; the solids portion from this process was extracted with a 50:50 mixture of toluene/(IPA) (ratio of 1 Kg solids to 4 L solvent) several times until the solvent was reasonably clear. After air drying, a portion of cleaned solids was dispersed in deionized water, freeze dried and called solids I.

A portion of solids I was cleaned with methylene chloride, air dried and freeze dried and called solids II. Finally, a portion of solids II was cleaned with methanol, dried and called solids III. A sample of sludge was just freeze dried in order to provide a sludge solids sample with its organics.

Characterization of Solids

Each of the solids types after the solvent treatment described gave different settling properties. Basically solids I and II, when redispersed in sludge water settled somewhat faster than the original sludge, but solids III settled much faster. Therefore, each was subjected to a preliminary examination by a number of techniques in order to determine how much and possibly the type of organic carbon that remains tightly bound to the solids. These techniques included total organic carbon (TOC), Fourier transform infrared (FTIR), thermogravimetric analysis (TGA), nuclear magnetic resonance (NMR) and XRD.

The TOC data of the original freeze dried sludge solids and each of solids I, II and III are given in Table 6. It can be seen that the initial solvent treatment essentially removes all the loosely bound organic material. The small changes in TOC in solids II and III may reflect a trace amount of solvent contamination, since a finite amount of organic material was removed with the methylene chloride. Practically no material was removed with the methanol. Unfortunately the weights of organic material were not recorded.

The FTIR spectra of the freeze dried solids and solids I, and that of china clay are shown in Figures 26 and 27. There is little absorption at 2925 cm^{-1} (the CH stretching region) in the clay sample, whereas all the sludge solids give peaks in this region. Since the peaks at 3621 and 3697 cm^{-1} appear to be due to clay (probably kaolinite), the relative organic content was estimated from the ratio of the areas of the CH to clay absorption peaks. The results for all solids samples are given in Table 6, and with the exception of solids I seem to follow the same trend as for TOC.

TABLE 6: Organic Content of Sludge Solids Before and After Solvent Treatment

Solids	TOC (wt%)	IR (relative peak ratios)	TGA (relative %)
Freeze-dried	9.70	0.29	3.48
Solids I	2.60	0.04	1.11
Solids II	2.76	0.15	1.28
Solids III	2.75	0.10	1.02

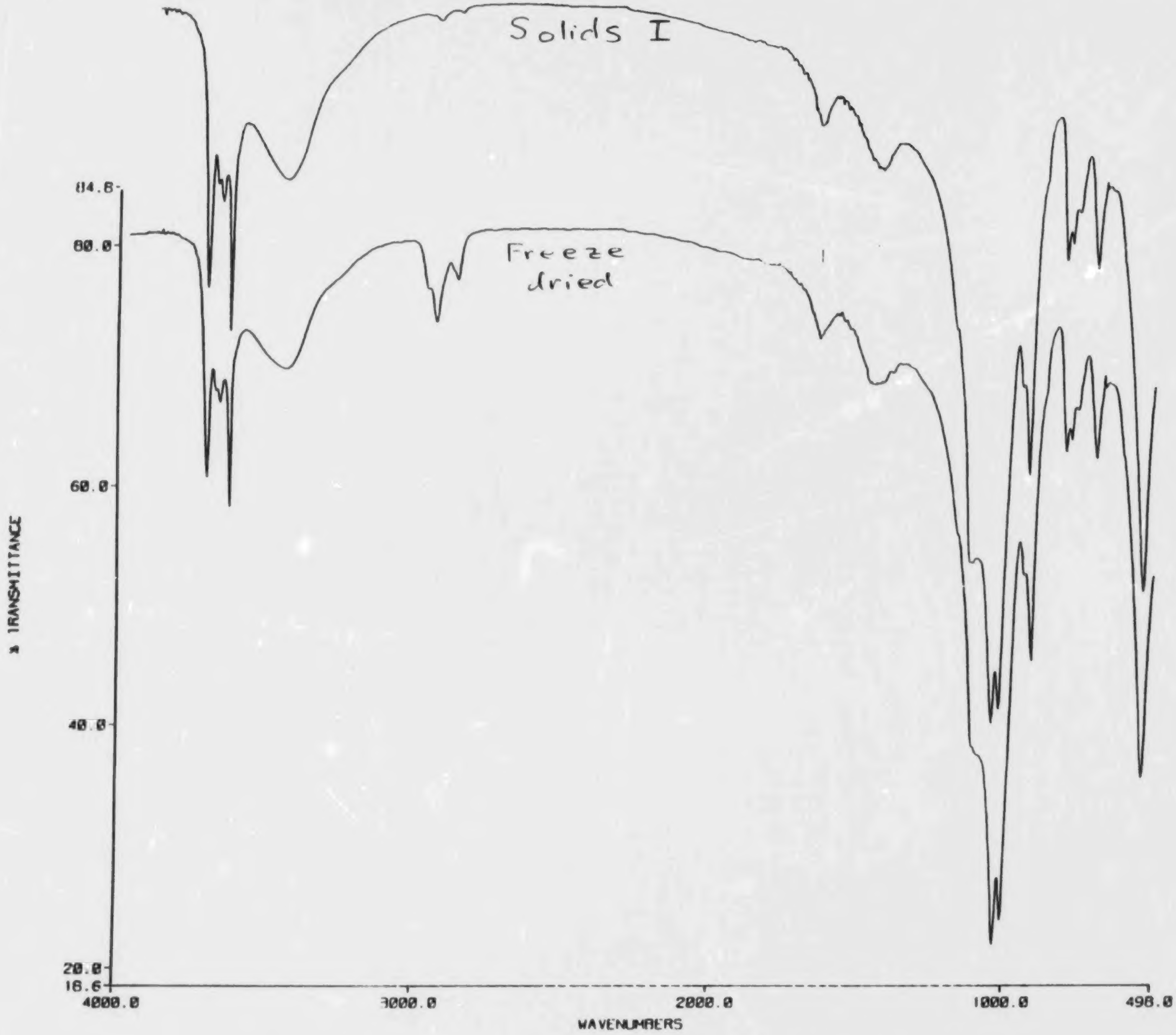


FIGURE 26: FTIR spectra of freeze dried solids and solids I

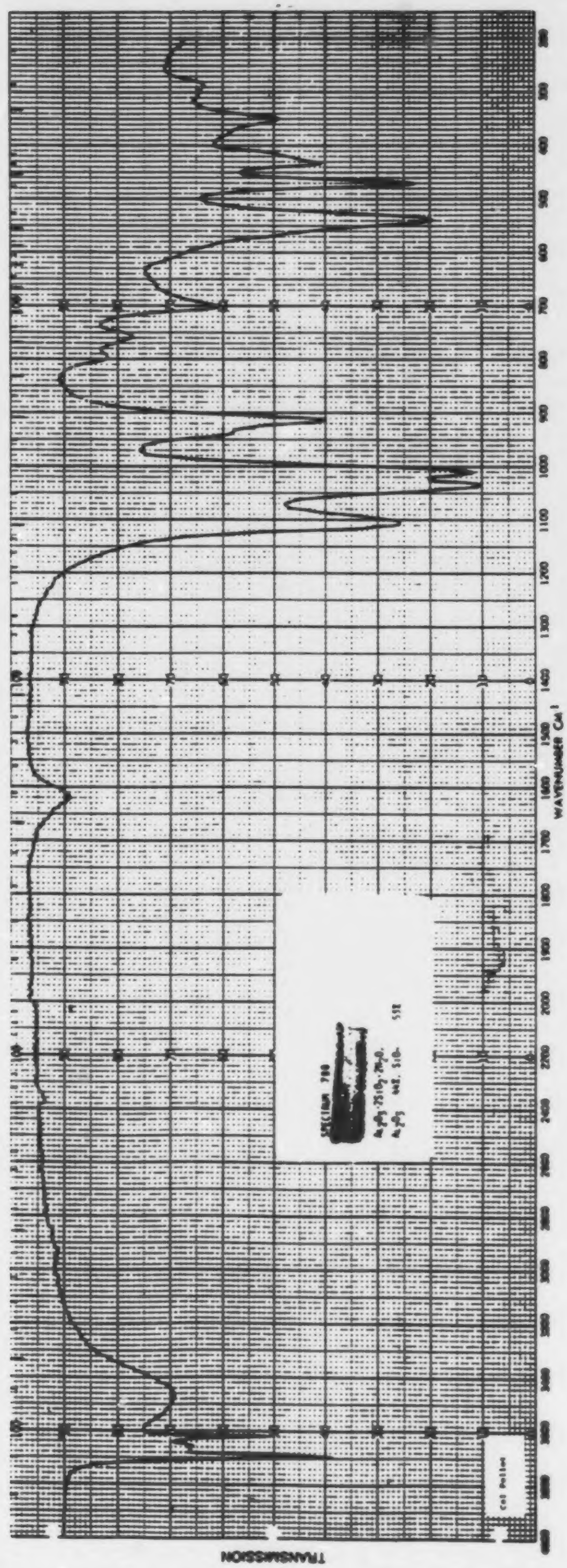


FIGURE 27: IR spectrum of China clay

TGA traces of all the solids samples are shown in Figure 28. The runs were carried out in a N_2 atmosphere up to 900°C. Qualitatively these scans indicate that the freeze dried solids contain more organic material than the solvent treated solids, consistent with the TOC results. In order to combust all remaining organic material (fixed carbon) after heating in the N_2 atmosphere, O_2 was introduced. The O_2 experiments are not shown in Figure 28. These experiments resulted in the relative organic carbon contents shown in Table 6. These results basically exhibit the same trend as the TOC.

An unsuccessful attempt was made to obtain an NMR spectrum of the residual organic material on the solids samples. There was too little organic material to give a reasonable spectrum.

An XRD study was carried out on the four solids samples by F. Longstaffe (1). The spectra are shown in Figures 29 to 32, and the semi-quantitative results given in Table 7. No significant differences in mineralogy were observed among the samples. In particular, no mineralogical feature was observed which could explain the difference in settling characteristics of solids III compared to the others. In terms of clay mineral crystallinity, the results in Table 7 indicate a modest increase in illite crystallinity following removal of organic matter (lower value in 10A-Xtal for the freeze dried compared to the others). The results for kaolinite, however, are ambiguous and could even suggest that solvent treatment led to a slight decrease in crystallinity, but this is far from definitive. In summary, no dramatic difference in clay mineral crystallinity was evident among the samples for either illite or kaolinite. Perhaps the different settling behavior is related to a small amount of the organic matter retained on the mineral surfaces during the solvent treatments.

Characterization of Extracted Organics

The organic material extracted with toluene/IPA, organics I, was the only material characterized because of the negligible amounts obtained from the other solvent extractions. Organics I appeared very much like bitumen. The asphaltene content (n-pentane insolubles) was 19.0 wt%. This value is somewhat higher than the typical Athabasca bitumen value of 17 wt% (6), but could be due to some oxidation of the bitumen in the sludge.

The asphaltenes from the organic I material were fractionated by size exclusion chromatography (SEC) using Biobeads SX1, and the results compared to a Cold Lake bitumen. The typical asphaltene content of this bitumen is 15 wt% (6). The SEC results are shown in Table 8. The highest molecular weight (largest size) materials are eluted from the column first and have the lowest fraction numbers. In view of the standard deviations for the Cold L. samples, there is really no difference in the size distribution between the sludge and Cold L. asphaltenes.

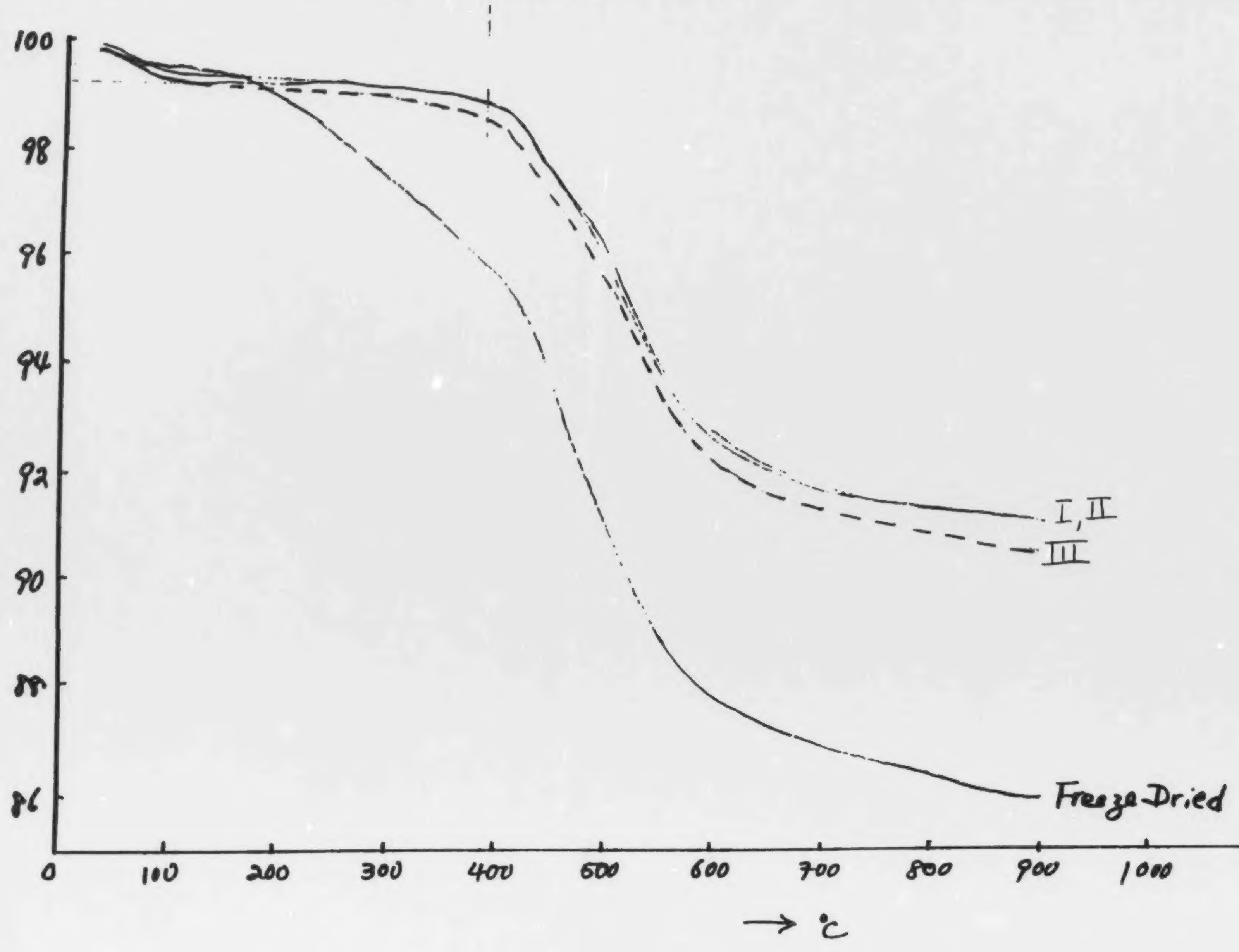


FIGURE 28: TGA traces of sludge solids

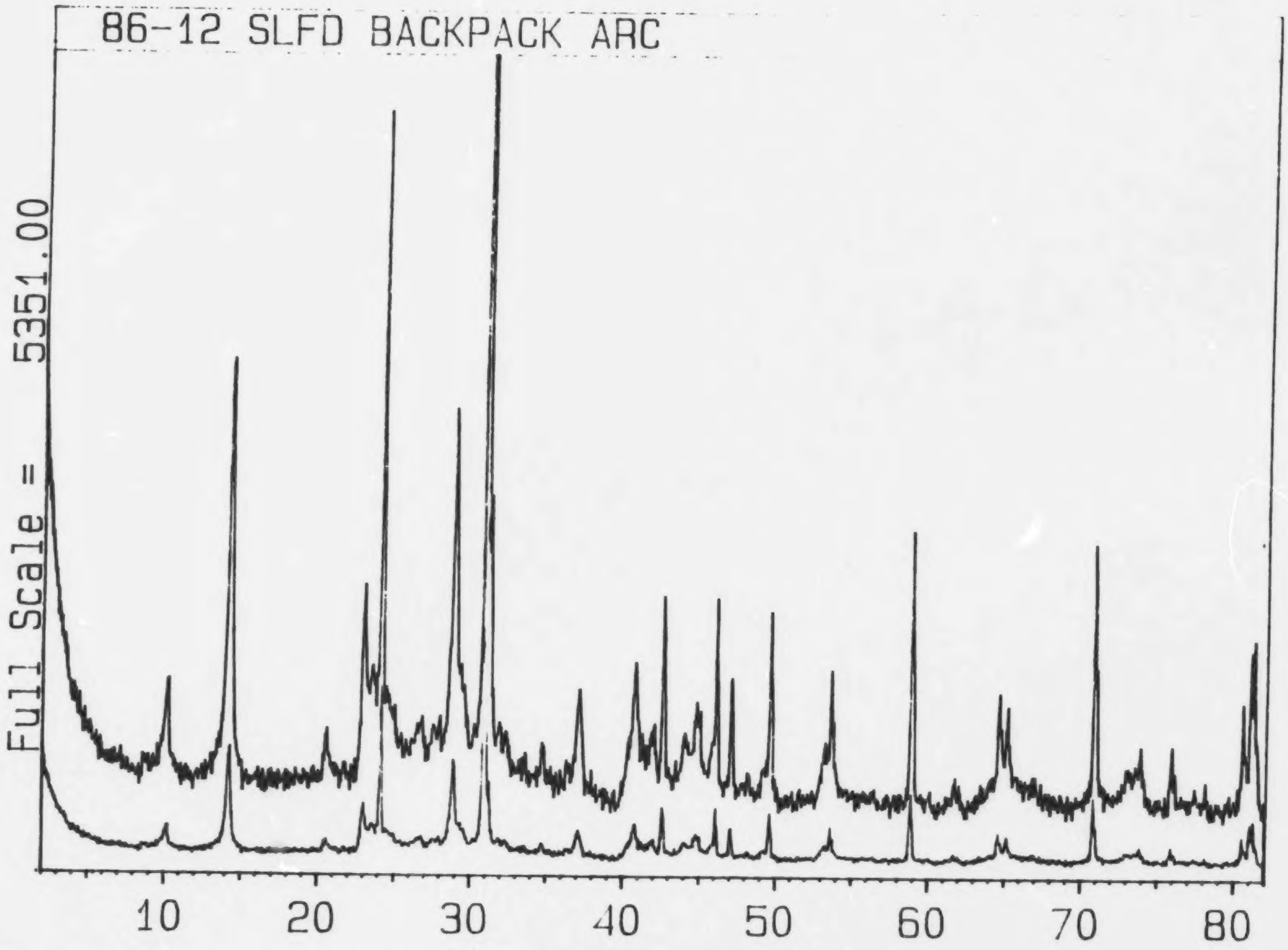


FIGURE 29: Diffractogram of freeze dried solids

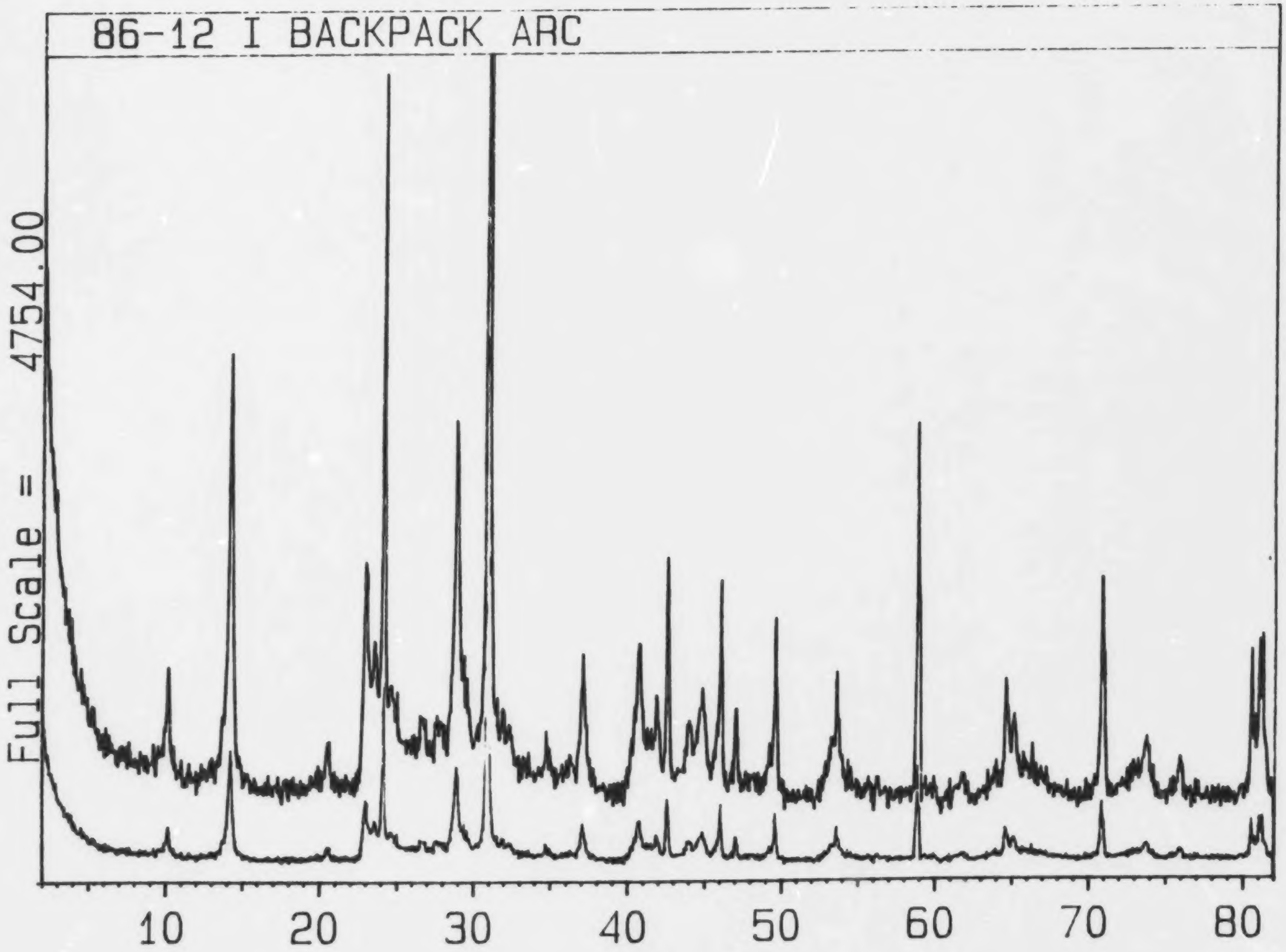


FIGURE 30: Diffractogram of solids I

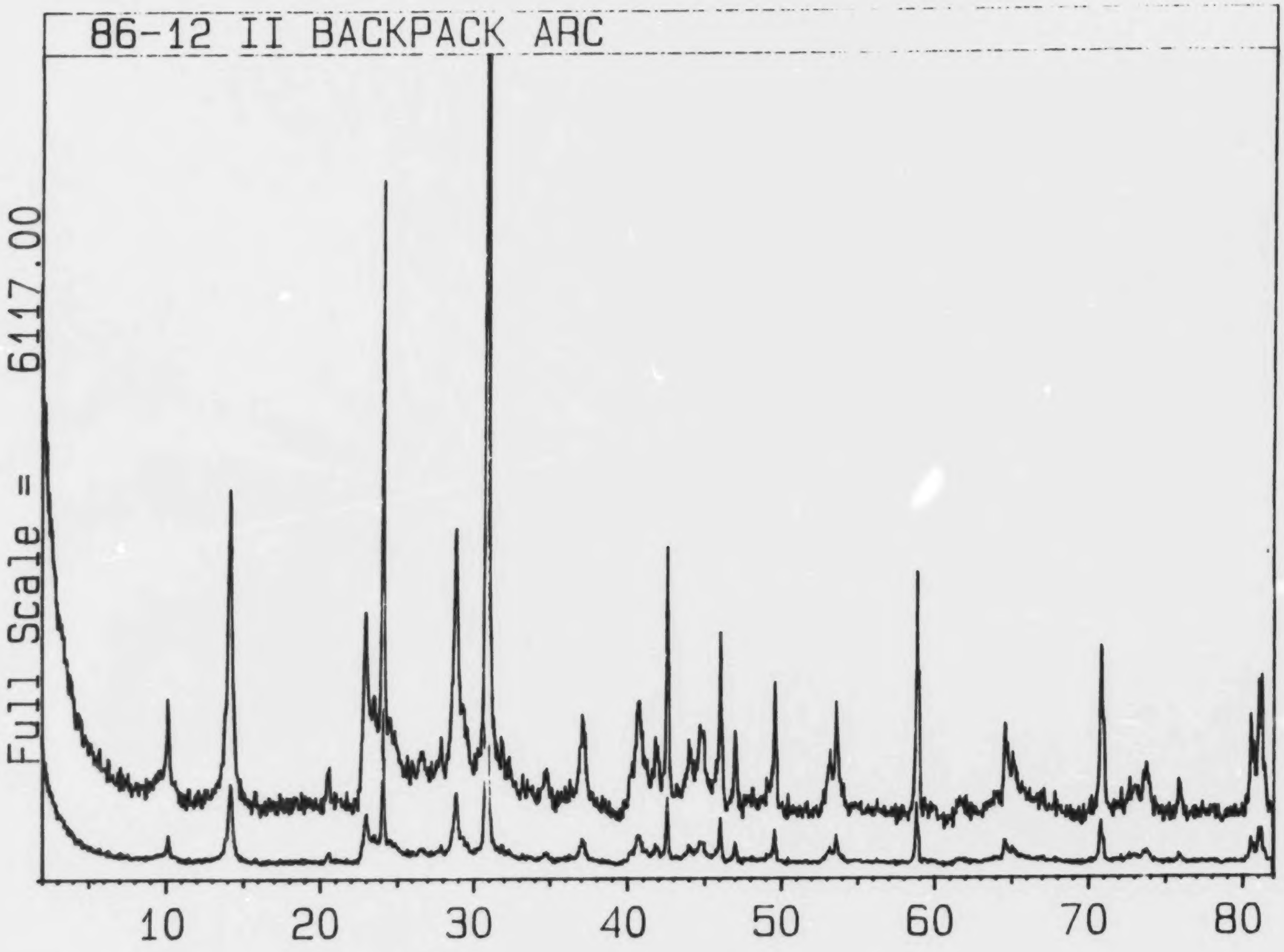


FIGURE 31: Diffractogram of solids II

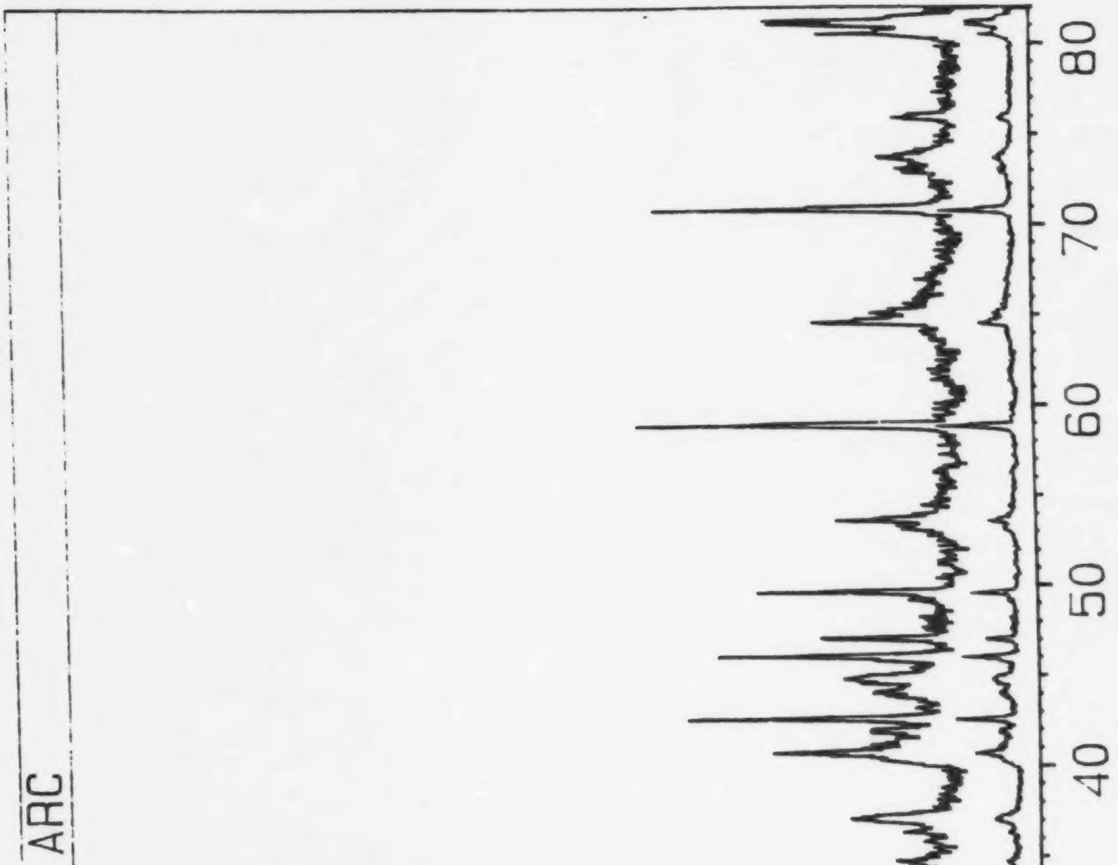


FIGURE 32: Diffractogram of solids III

TABLE 7: Semi-quantitative X-Ray Diffraction Analysis of Sludge Solids

Fraction	I	K**	Qtz	KF	PI	Sid	Cal	10Å-Xtal	7Å-Xtal
Freeze-dried	5.7%	11.2%	77.9%	0.8%	0.7%	2.7%	1.1%	7.00	27.67
Solids I	6.2%	11.1%	75.9%	1.2%	0.8%	3.7%	1.1%	10.00	20.00
Solids II	5.6%	8.0%	81.6%	0.5%	1.0%	2.6%	0.7%	11.50	18.57
Solids III	6.0%	8.6%	80.0%	0.8%	1.3%	2.2%	1.0%	11.50	22.00

I = illite; K = kaolinite; Qtz = quartz; KF = K-feldspar; PI = plagioclase; Sid = siderite; Cal = calcite; 10A-Xtal = measure of crystallinity of illite; 7A-Xtal = measure of crystallinite of kaolinite.

*Values reported are weight peak heights only, not weight percent.

**Includes minor chlorite and/or berthierine.

TABLE 8: Results of Fractionation of Asphaltenes by Size Exclusion Chromatography (Biobeads Sx1)

	Weight Percentage of Fractions				
	1*	2	3	4	5
Sludge	16	37	23	14	15
Cold Lake*	17±4	35±5	23±4	16±6	13±2

* Fraction 1 has the highest molecular weight, fraction 5 lowest

** Average of six experiments

TABLE 9: Proton Aromaticities of SEC Fractions

	1	2	3	4	5
Sludge	10	11	14	23	34
Cold Lake*	13	15	20	24	40

The proton NMR aromaticity results for each fraction of each of the asphaltenes are shown in Table 9. These results indicate a consistently lower proton aromaticity for the sludge as compared to the Cold L. asphaltenes.

Summary

The TOC, IR and TGA data are all useful for indicating the amount of residual organic material on sludge solids. However, none provides any indication of any differences between solids I, II and III which could explain their different settling behavior. There are no structural differences of an inorganic nature as studied by XRD which may be responsible for differences in among solids I, II and III. Perhaps the mineral surfaces retained a portion of solvent from the treatment which imparts a different wetting and subsequent settling behavior when the solids are redispersed in water.

The characterization results indicate that the loosely bound and easily removed organic material on the sludge is bitumen. It was shown to be similar to both Athabasca and Cold Lake bitumen. The slightly higher asphaltene content of the sludge bitumen, however, indicates that it may be somewhat more oxidized than a typical solvent extracted Athabasca or Cold Lake bitumen. This may have occurred in the tailings pond, or may reflect the fact that in the hot water process the asphaltenes containing more of the carbonyl groups could be the ones which tend to become attached to the sludge forming solids.

CONCLUSIONS

A satisfactory subsampling procedure was developed for obtaining Syncrude tailings pond sludge for this study. This sludge has a solids content of 28 wt%, and of these solids 90 wt% are less than 37 μ in size, while 30 wt% are less than 2 μ, or clays. X-ray diffraction analysis indicated that quartz, kaolinite and illite are predomonant, the latter two clays increasing in proportion in the smaller particle size fractions. The water chemistry is dominated by dissolved NaCl and $NaHCO_3$ at pH 8, with a significant amount of total organic carbon. Rheological data obtained on whole sludge indicated that it has a definite structure which appears to depend on its shear history.

Addition of NaCl to the sludge results in flocculation and an increase in its structure as indicated by the large overshoot stress in its rheological curves. Between 0.08 and 0.12 M salt concentration the extent of flocculation is at a maximum which corresponds to a destabilization. The rheology data is consistent with centrifugation tests, short term settling experiments and electrokinetic analysis.

Following treatment with a number of organic solvents, the redispersed sludge solids exhibited enhanced settling properties. The amount of residual organic material on these solids could be measured by total organic carbon analysis, infrared and thermogravimetric analysis. None of these techniques nor x-ray diffraction could distinguish between the solvent treated solids in order to explain their differences. The loosely bound organic material removed by treatment with toluene/i-propyl alcohol is basically bitumen, but somewhat more oxidized than typical oil sand extracted bitumen.

REFERENCES

1. Longstaffe, F.J., "X-ray Diffraction Analyses of Sludge Solids", Report prepared for Alberta Research Council, June 30, 1989.

2. Ignasiak, T.M., Kotlyar, L., Longstaffe, F.J., Strausz, O.P. and Montgomery, D.S., Fuel **62**(1983)353.

3. Goodeve, C.F., Trans. Faraday Soc. **35**(1939)342.

4. Gillespie, Th., J. Colloid Sci. **15**(1960)219.

5. Tadros, Th.F. (Ed), "Solid/Liquid Dispersions" Academic Press, London (1987).

6. Selucky, M.L., Chu, Y., Ruo, T.C.S. and Strausz, O.P., Fuel **57**(1978)9.

APPENDIX 1

RHEOGRAMS OF SLUDGES WHICH SAT IN THE CYLINDER THE INDICATED TIMES PRIOR TO IMMERSING THE ROTOR

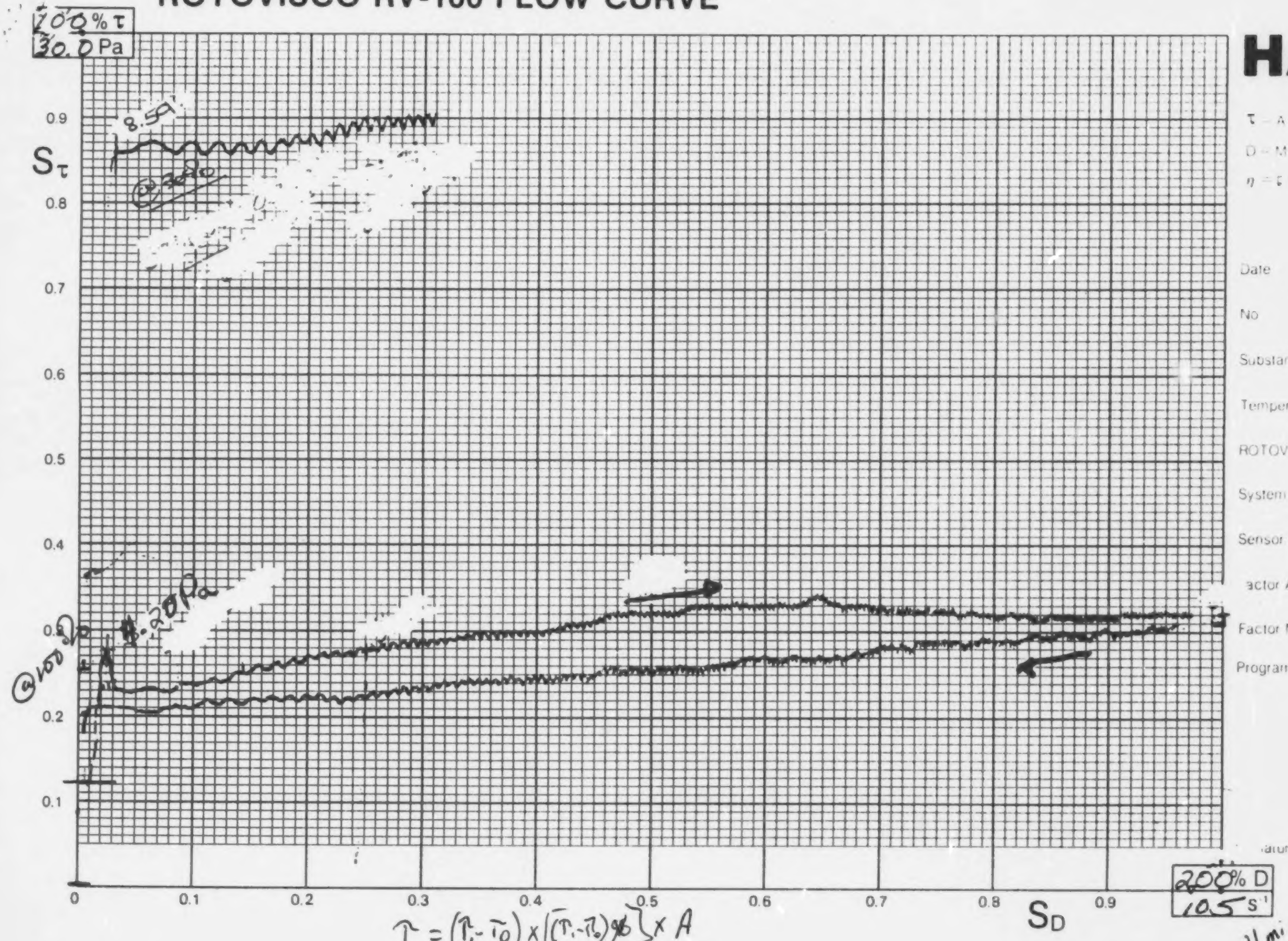
ROTOVISCO RV-100 FLOW CURVE

HAAKE

$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]

$D = M \cdot \%D \cdot S_D$ [s^{-1}]

$\eta = \tau / D$ [Pa·s]



100rpm/min

$\tau = (\tau_i - \tau_0) \times [(\tau_i - \tau_0)\%] \times A$

$\eta = [(\tau_i - \tau_0)\%] \times G / S_D(\text{rpm})$

Date	
No	1
Substance	0 min
Temperature	
ROTOVISCO RV	3
System	MK50
Sensor system	MV I
actor A Pa	0.300
Factor M	0.525
Program times	
T_1	
T_2	
T_3	
ature	

Order No 10-87-911

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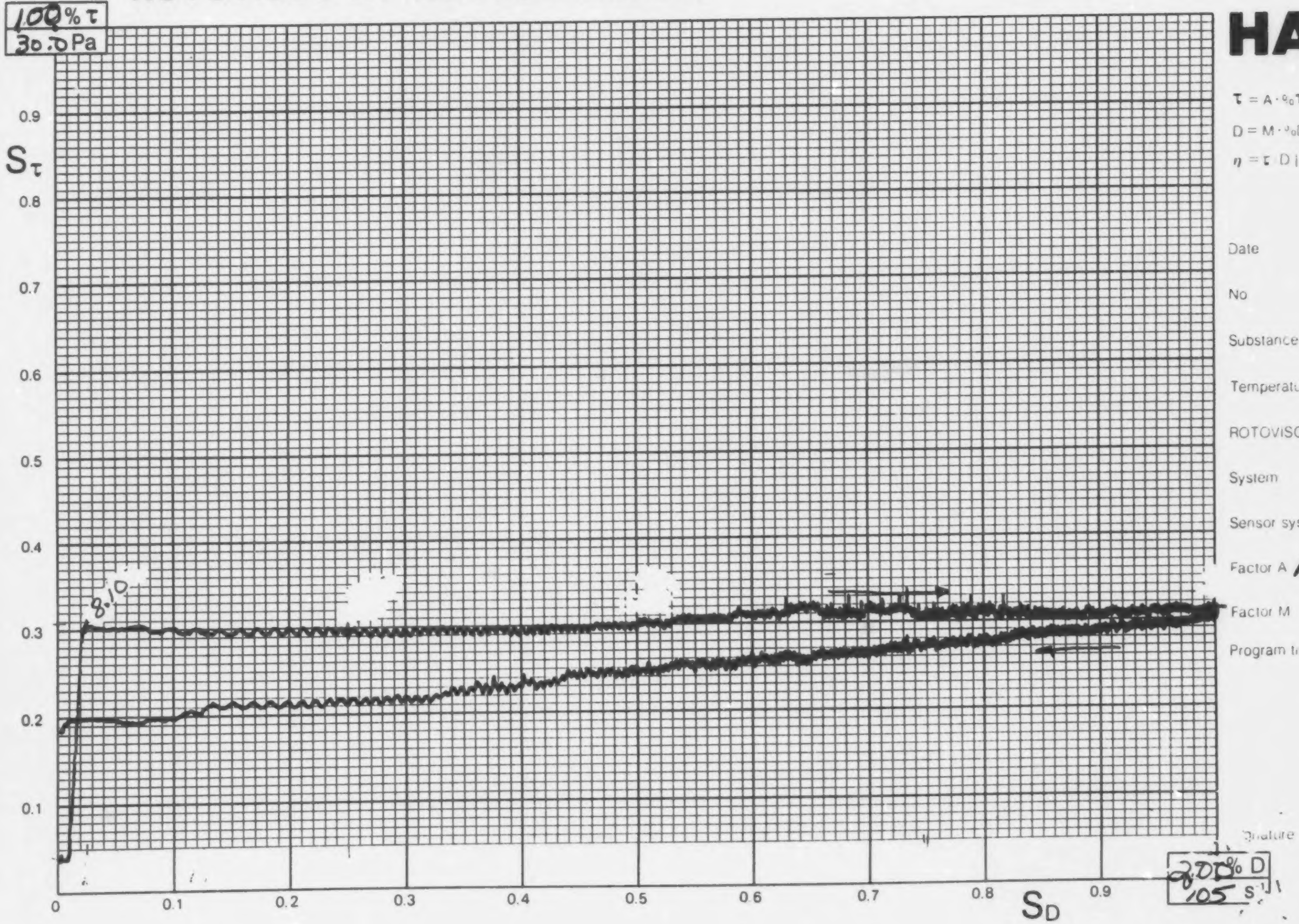
ROTOVISCO RV-100 FLOW CURVE



HAAKE

$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]

$D = M \cdot \%D \cdot S_D$ [s^{-1}]

$\eta = \tau / D$ [Pa·s]

Date	
No	2
Substance	1 min
Temperature	
ROTOVISCO RV	3
System	MK500
Sensor system	MV I
Factor A Pa	0.300
Factor M	0.525
Program times	
T₁	
T₂	
T₃	
Signature	

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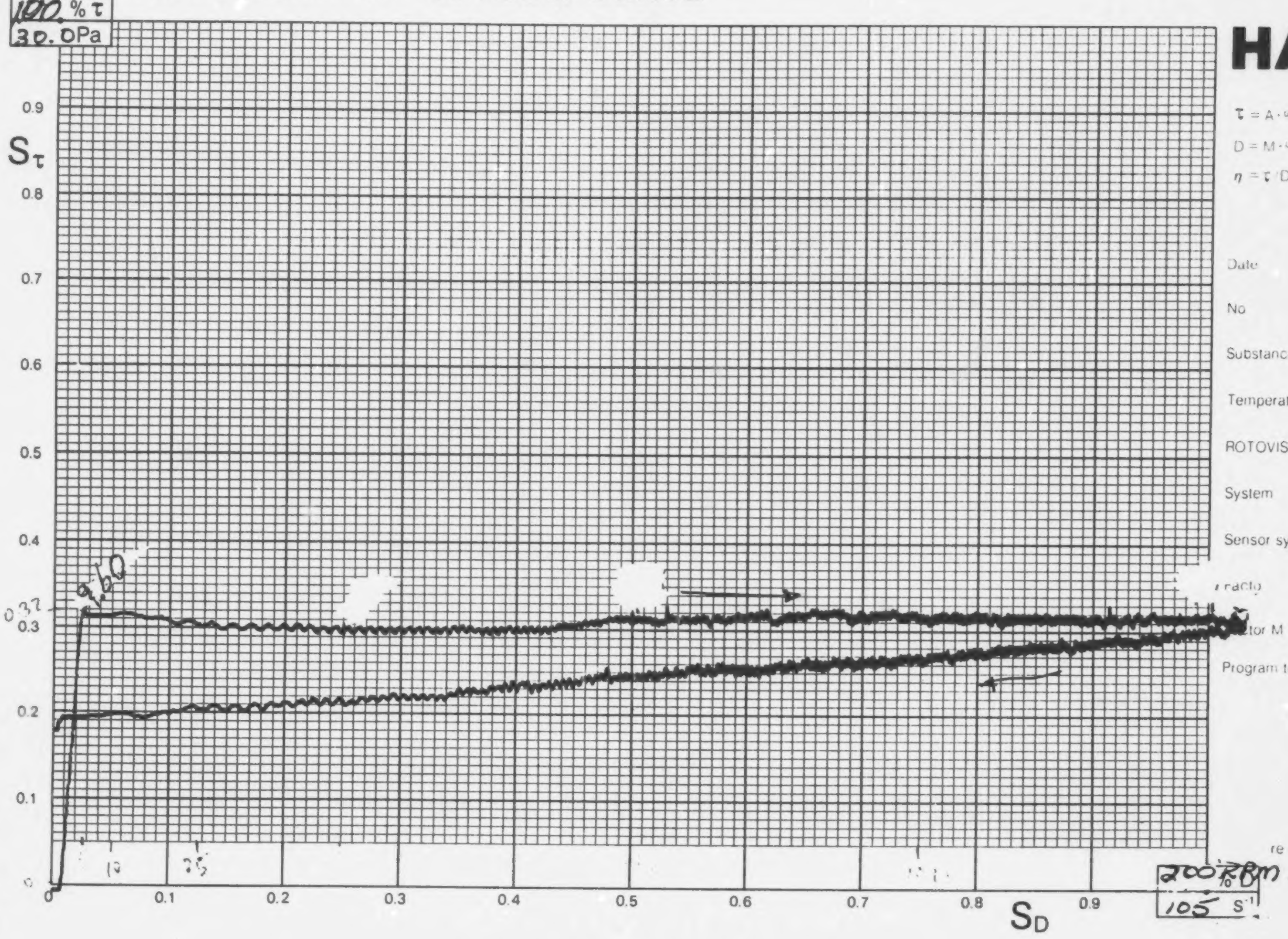
RV 847A 1P

ROTOVISCO RV-100 FLOW CURVE



HAAKE

$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]

$D = M \cdot \%D \cdot S_D$ [s^{-1}]

$\eta = \tau / D$ [Pa·s]

Date
No 3
Substance 22min
Temperature
ROTOVISCO RV 3
System MK50
Sensor system MV I
factor P. 0.300
factor M 0.525
Program times
T1
T2
T3
re

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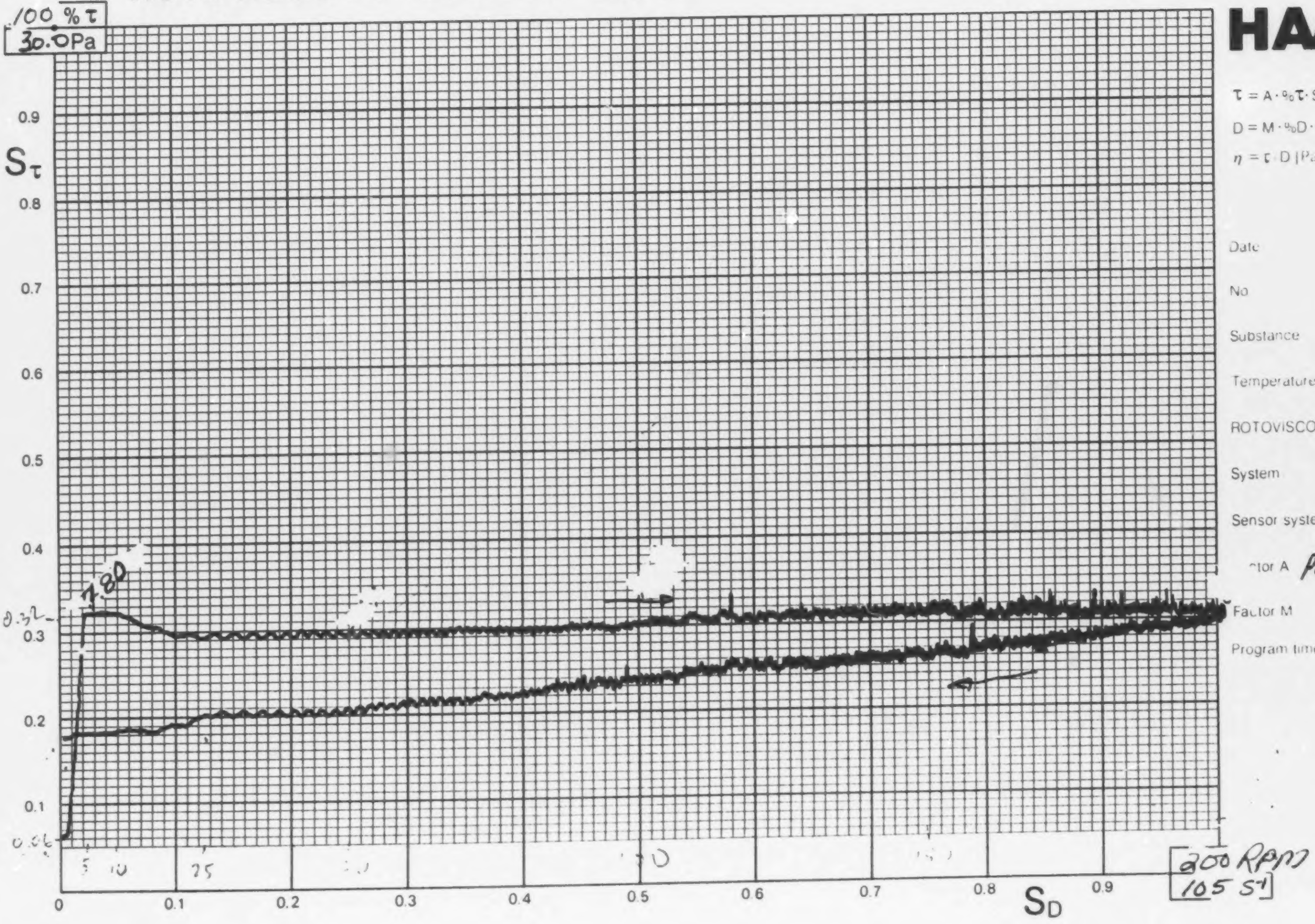
ROTOVISCO RV-100 FLOW CURVE



HAAKE

$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]

$D = M \cdot \%D \cdot S_D$ [s⁻¹]

$\eta = \tau : D$ [Pa·s]

Date	
No	4
Substance	45min
Temperature	
ROTOVISCO RV	3
System	MK50
Sensor system	MV-I
Factor A ρ_a	0.300
Factor M	0.6255
Program times	
T_1	
T_2	
T_3	

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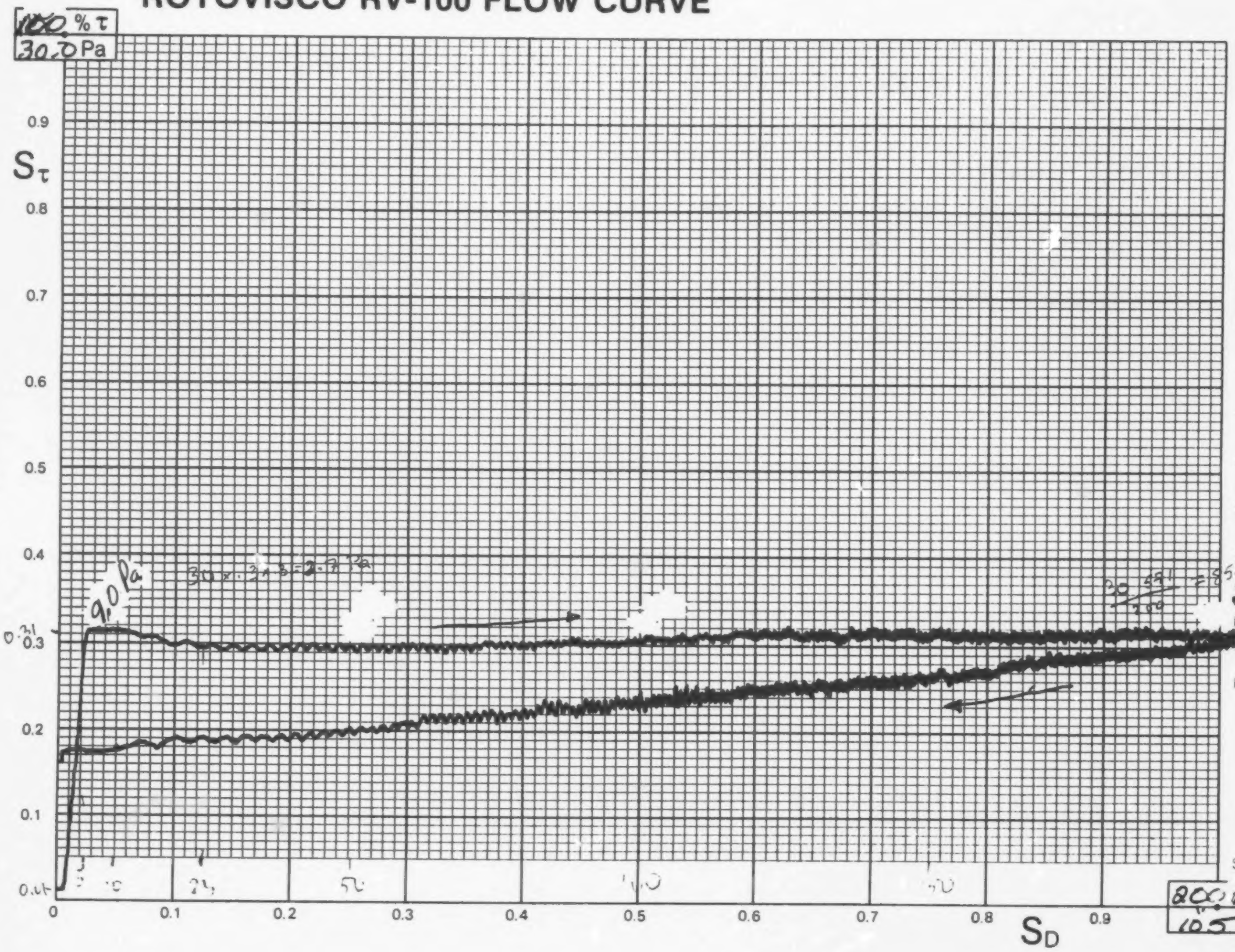
RV 847A

ROTOVISCO RV-100 FLOW CURVE



HAAKE

$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]
$D = M \cdot \%D \cdot S_D$ [s^{-1}]
$\eta = \tau / D$ [Pa·s]

Date	
No	5
Substance	90 min
Temperature	
ROTOVISCO RV	3
System	mk50
Sensor system	MVI
Factor A Pa	0.300
Factor M	0.5256
Program times	
T_1	
T_2	
T_3	
Signature	

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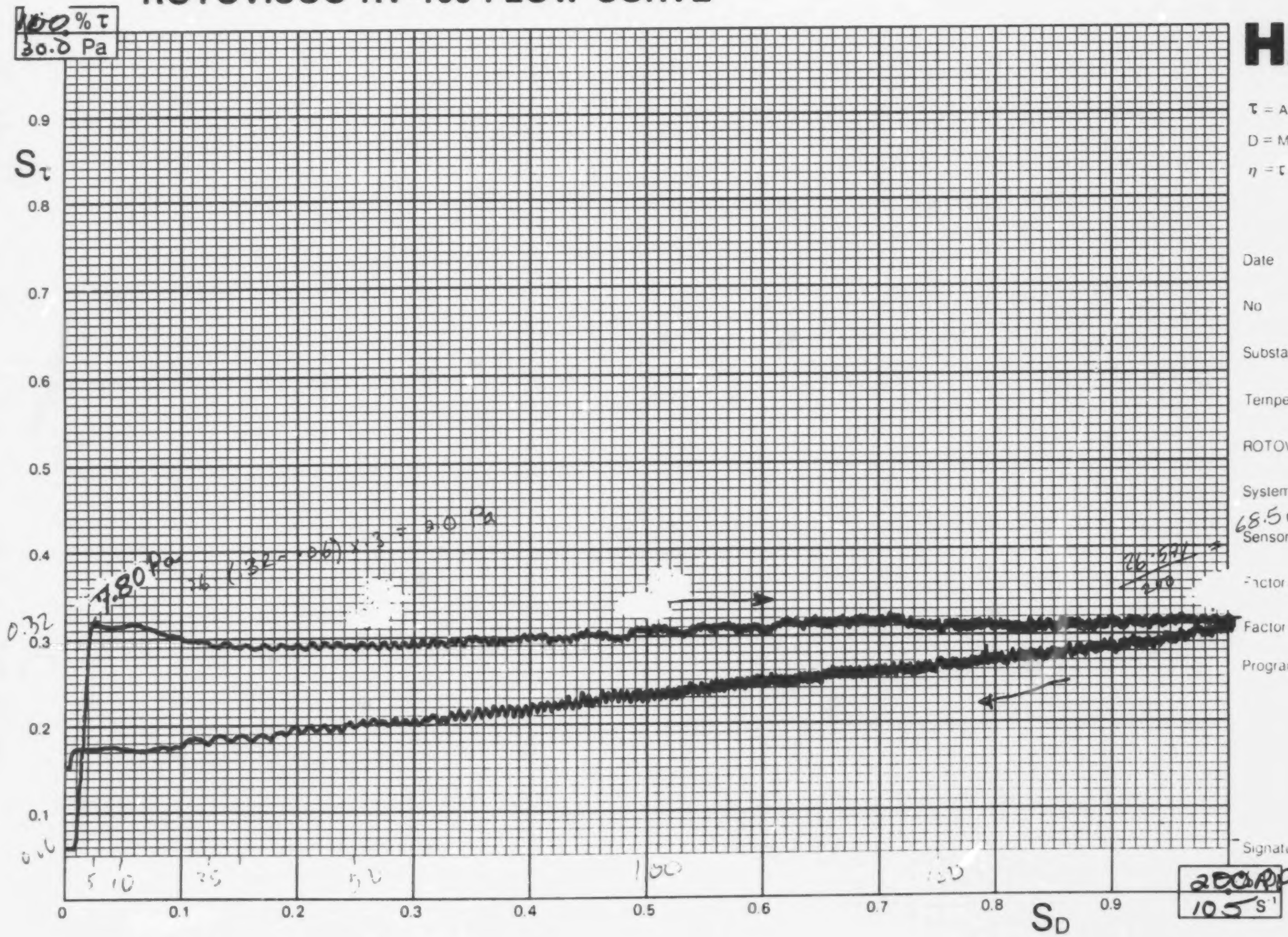
RV 847A 11

ROTOVISCO RV-100 FLOW CURVE

HAAKE

$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]
$D = M \cdot \%D \cdot S_D$ [s^{-1}]
$\eta = \tau : D$ [Pa·s]



Date
No 6
Substance 3 M
Temperature
ROTOVISCO RV 3
System MK50
68.5 mPa·s
Sensor system MV I
Factor A Pa 0.300
Factor M 0.5255
Program times
T_1
T_2
T_3
Signature

Order No 10-87-911

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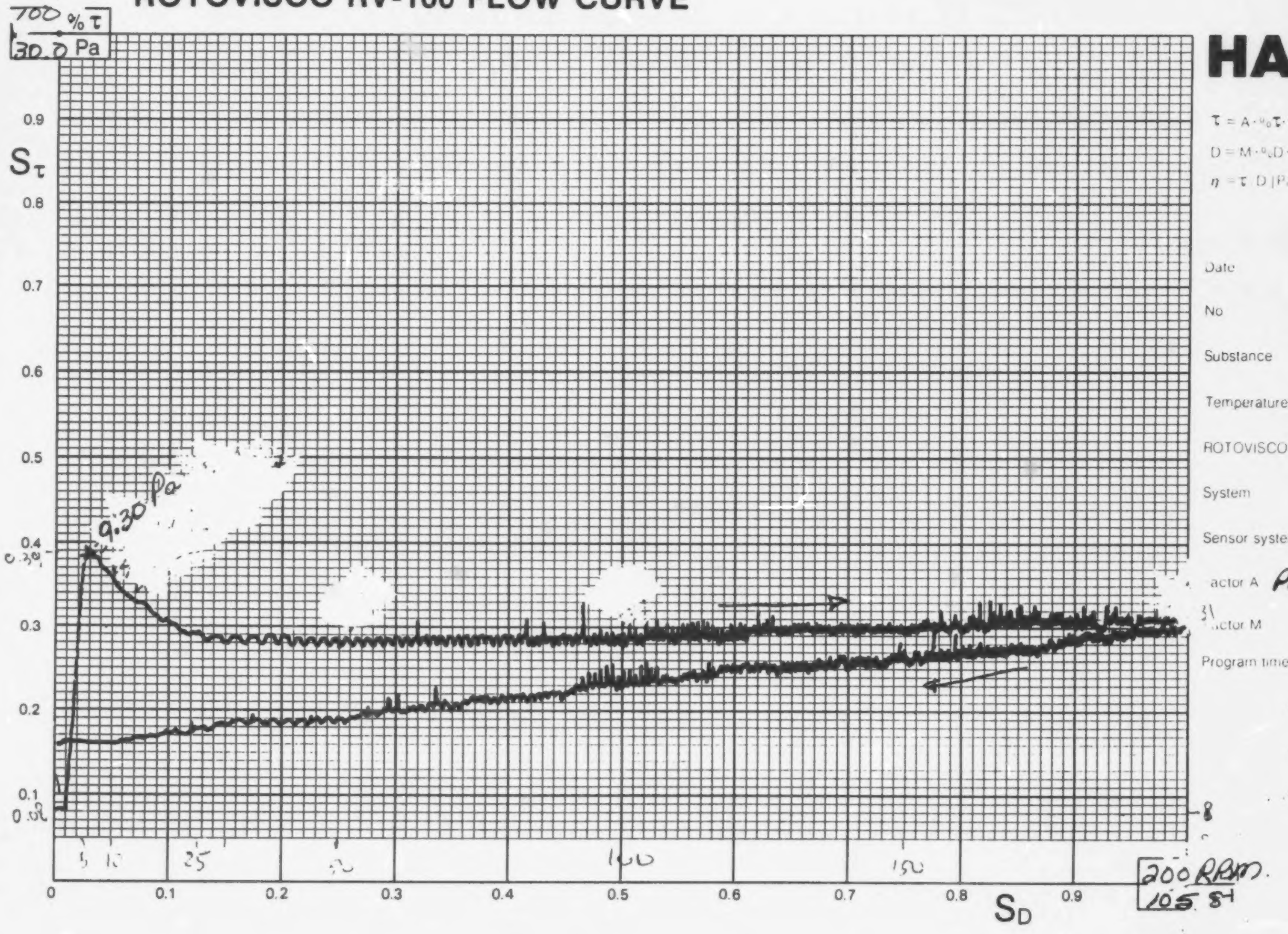
RV 847A 11

ROTOVISCO RV-100 FLOW CURVE



HAAKE

$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]

$D = M \cdot \%D \cdot S_D$ [s^{-1}]

$\eta = \tau : D$ [Pa·s]

Date	
No	7
Substance	6hr.
Temperature	
ROTOVISCO RV	3
System	MK50
Sensor system	MV I
Factor A Pa	0.300
Factor M	0.6255
Program times	
T_1	
T_2	
T_3	

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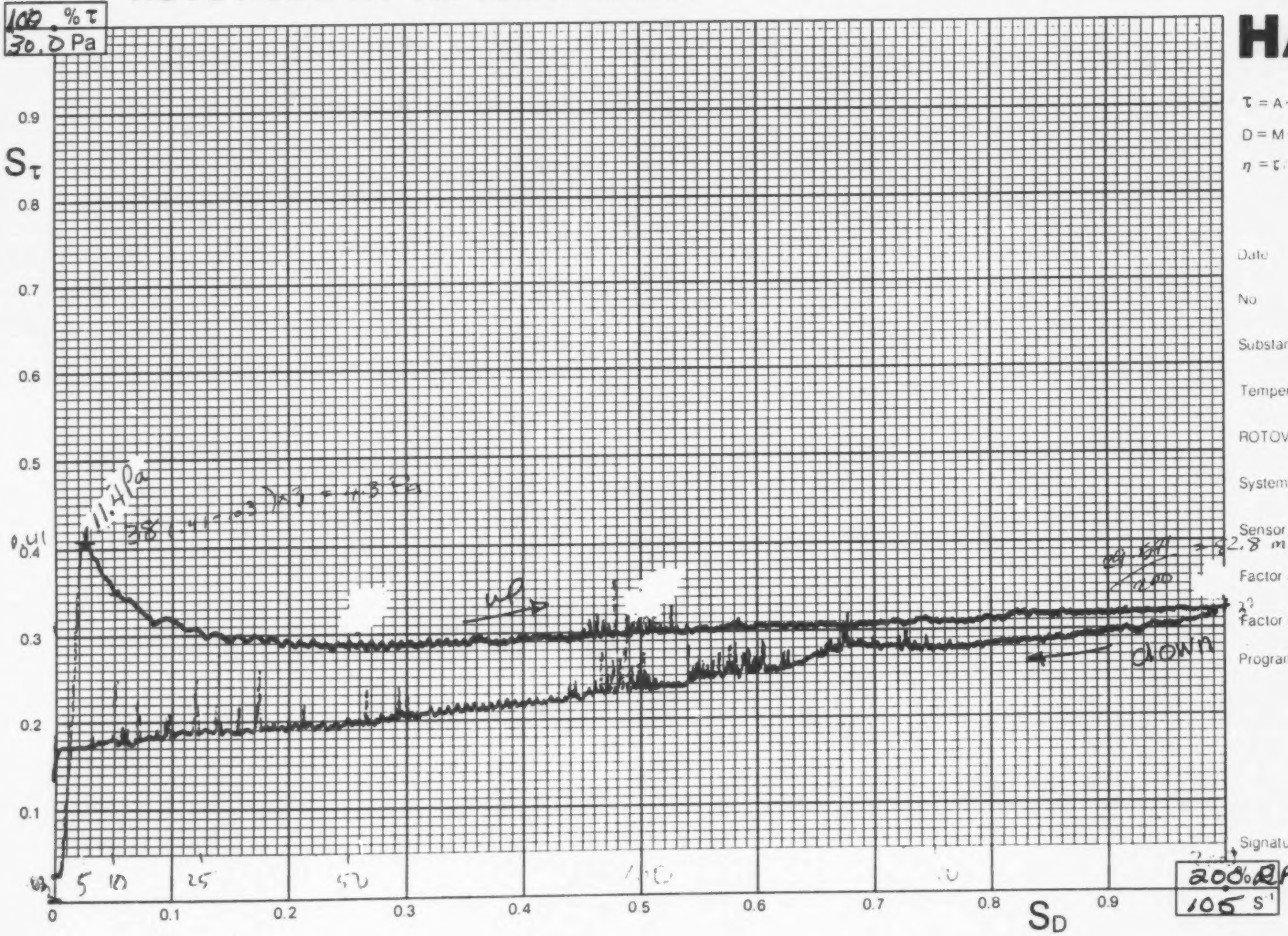
ROTOVISCO RV-100 FLOW CURVE



HAAKE

$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]
$D = M \cdot \%D \cdot S_D$ [s⁻¹]
$\eta = \tau / D$ [Pa·s]

Date
No 8
Substance 12 ms
Temperature [illegible]
ROTOVISCO RV 3
System MK50
Sensor system MV I
Factor A Pa 0.300
Factor M 0.5255
Program times
T₁
T₂
T₃
Signature

Order No 10-87 911

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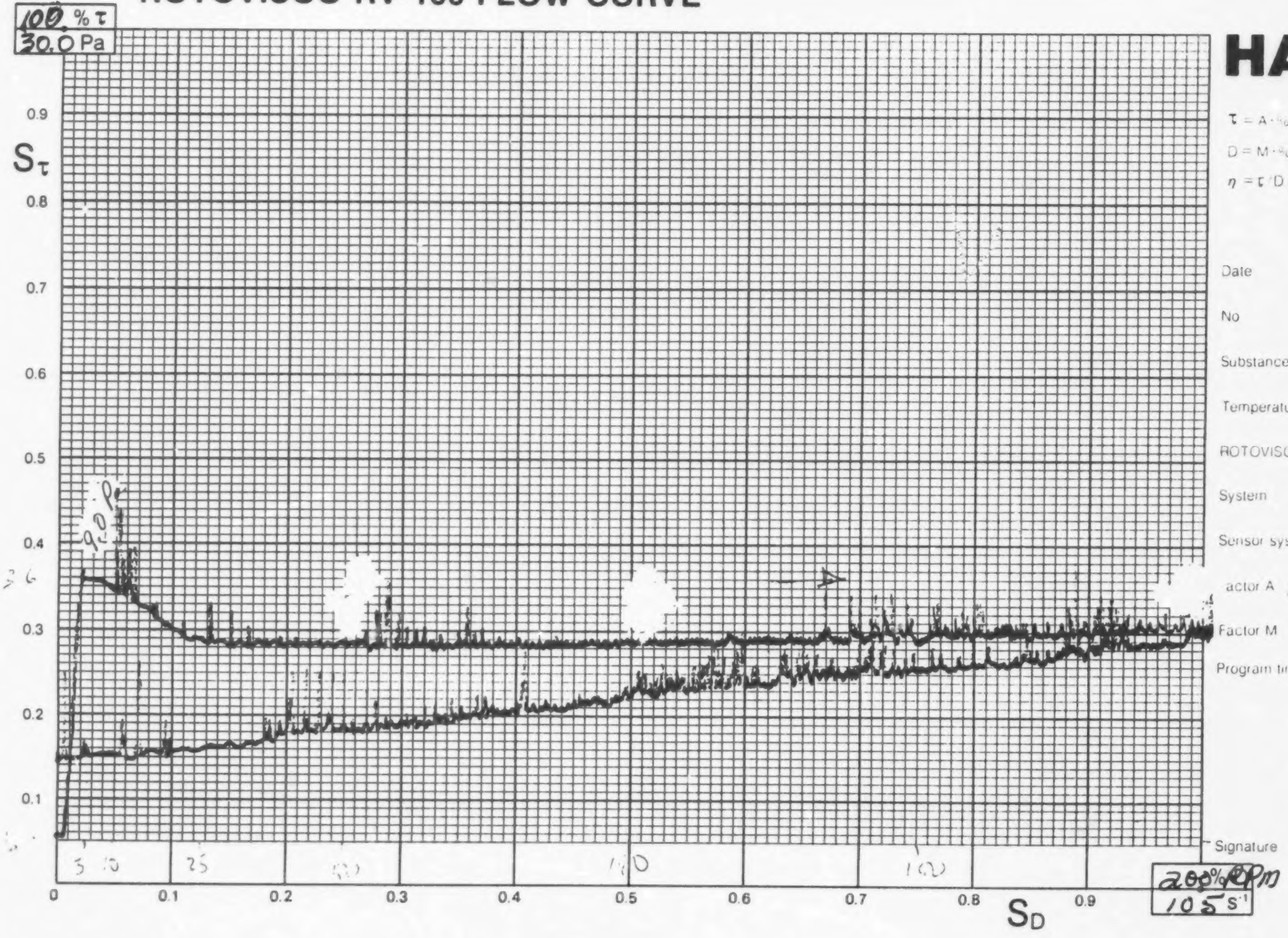
Rv 847A 1n

ROTOVISCO RV-100 FLOW CURVE

HAAKE



$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]

$D = M \cdot \%D \cdot S_D$ [s^{-1}]

$\eta = \tau / D$ [Pa·s]

Date	01/22
No	9
Substance	24hr.
Temperature	22.3
ROTOVISCO RV	3
System	MK50
Sensor system	MV I
actor A Pa	0.300
Factor M	0.5265
Program times	
T_1	
T_2	
T_3	
Signature	

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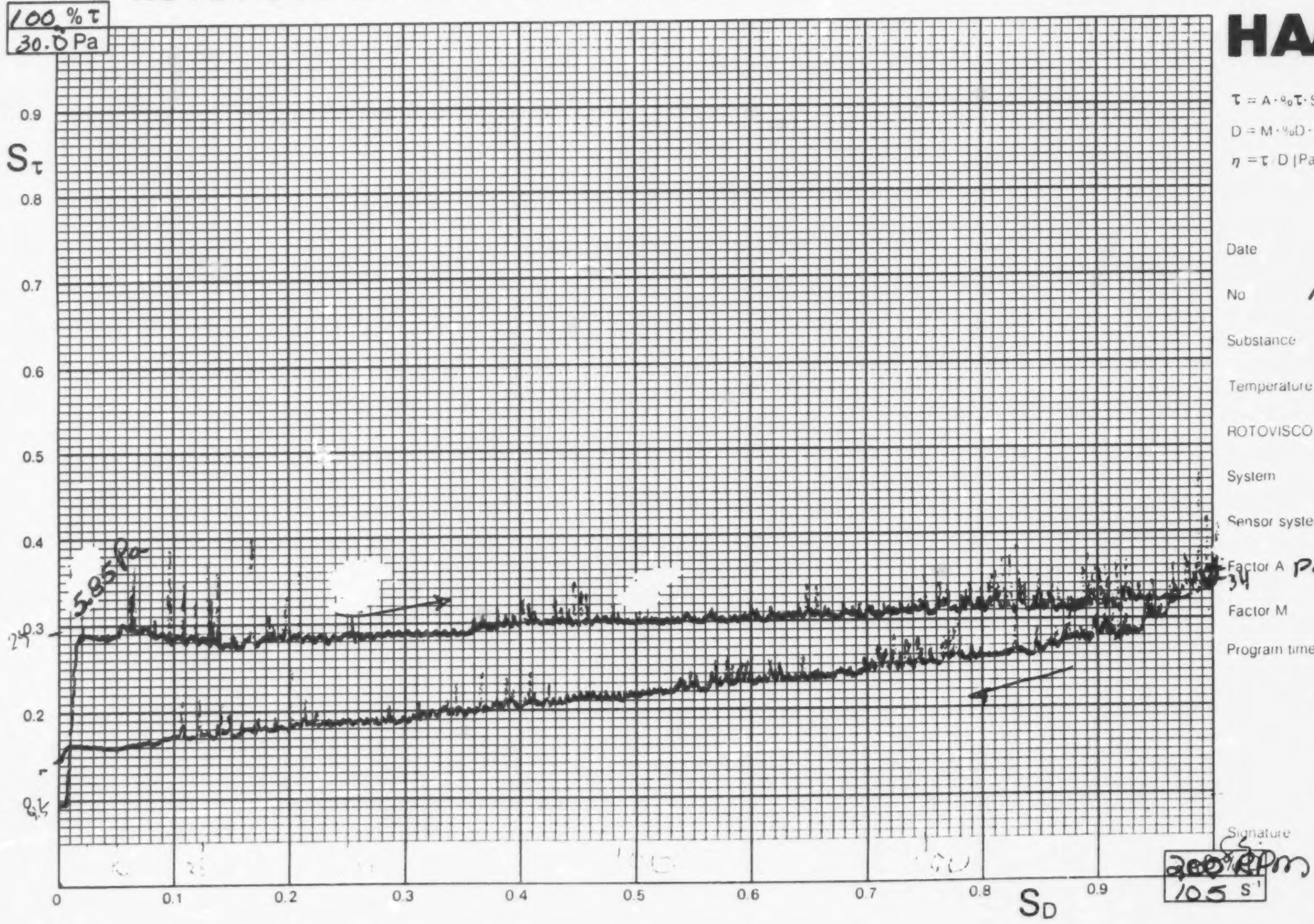
RV 847A 1/

ROTOVISCO RV-100 FLOW CURVE



HAAKE

$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]
$D = M \cdot \%D \cdot S_D$ [s⁻¹]
$\eta = \tau / D$ [Pa·s]

Date 01/23
No 10 48M. @49.5W
Substance
Temperature 21.1
ROTOVISCO RV 3
System MK50
Sensor system MV I
Factor A Pa 0.300
Factor M 0.5255
Program times
T₁
T₂
T₃
Signature

@50

@100

Order No 10 87 911

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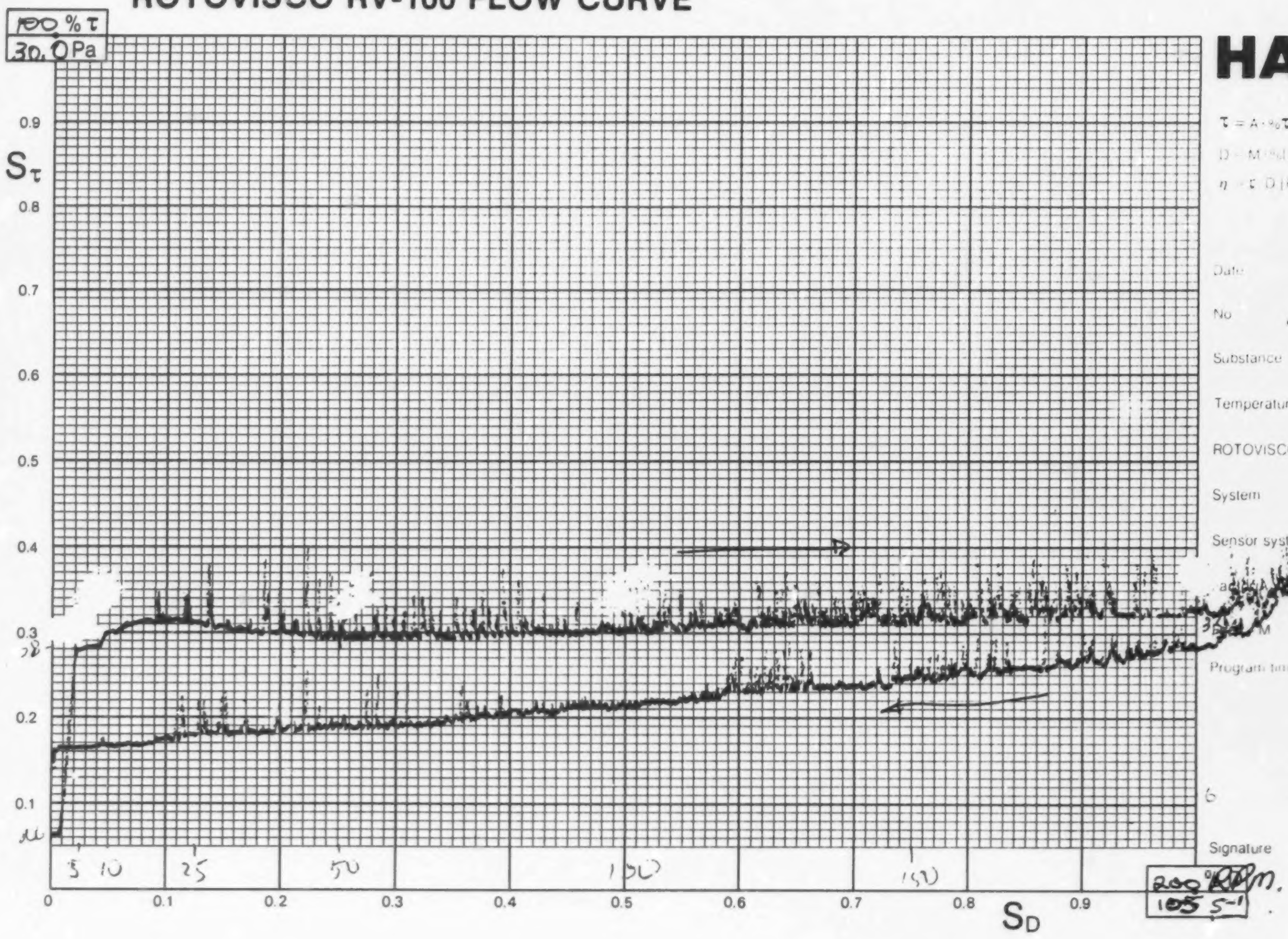
RV 847A 1c

ROTOVISCO RV-100 FLOW CURVE



HAAKE

$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]
$D = M \cdot \%D \cdot S_D$ [s^{-1}]
$\eta = \tau : D$ [Pa·s]

Date	01/25
No 11	4DAY
Substance	
Temperature	22° C.
ROTOVISCO RV	3
System	MK50
Sensor system	MV I
[illegible] A	0.300
[illegible] M	0.5255
Program times	
T_1	
T_2	
T_3	
Signature	

6

Order No 10 87 911

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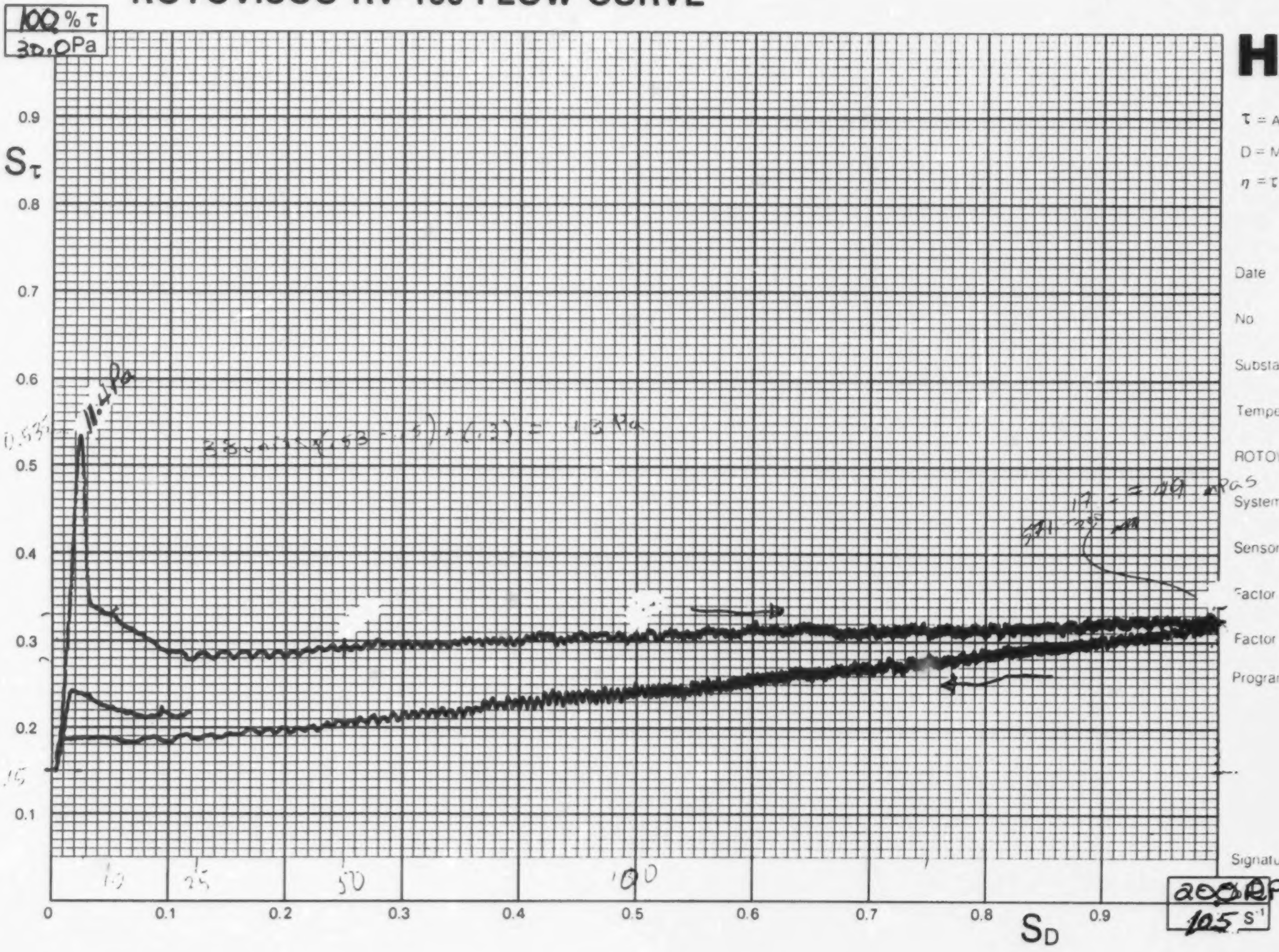
APPENDIX 2

RHEOGRAMS OF SLUDGES WHICH SAT IN THE CYLINDER THE INDICATED TIMES WITH THE ROTOR IMMERSED

ROTOVISCO RV-100 FLOW CURVE

sit 1hr (after 90min run.)



HAAKE

$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]

$D = M \cdot \%D \cdot S_D$ [s^{-1}]

$\eta = \tau / D$ [Pa·s]

Date

No 55.

Substance

Temperature

ROTOVISCO RV3

System MK50

Sensor system MVI

Factor A (R) 0.300

Factor M 0.5255

Program times

T₁

T₂

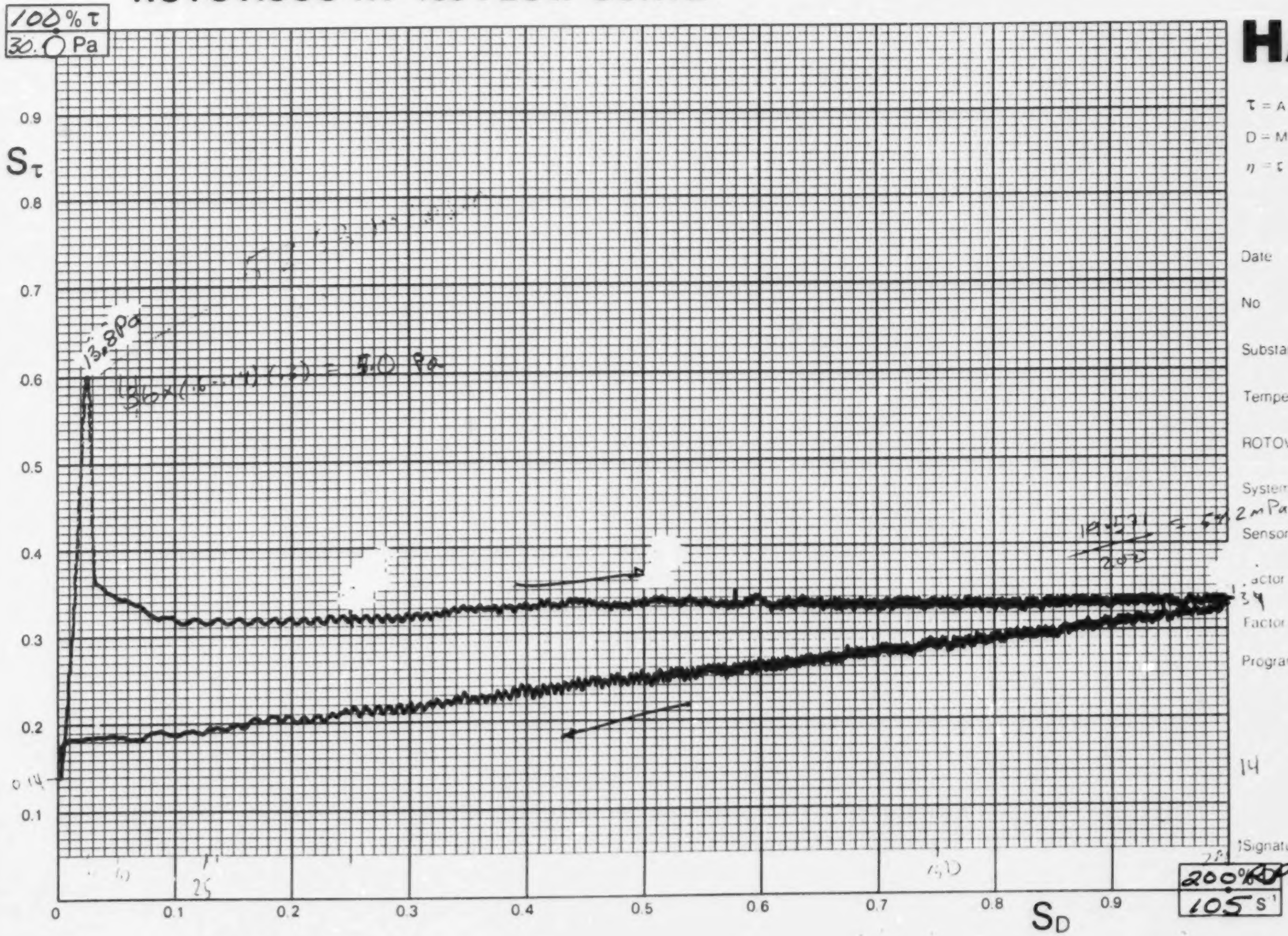
T₃

Signature

100 sec⁻¹

sit 2hr (after 2hr. run)

ROTOVISCO RV-100 FLOW CURVE



HAAKE

$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]
$D = M \cdot \%D \cdot S_D$ [s⁻¹]
$\eta = \tau : D$ [Pa·s]

Date
No 65
Substance
Temperature
ROTOVISCO RV3
System MK50
Sensor system MV I
Factor A Pa 0.302
Factor M 0.529
Program times
T₁
T₂
T₃
Signature

Order No. 10.87.911

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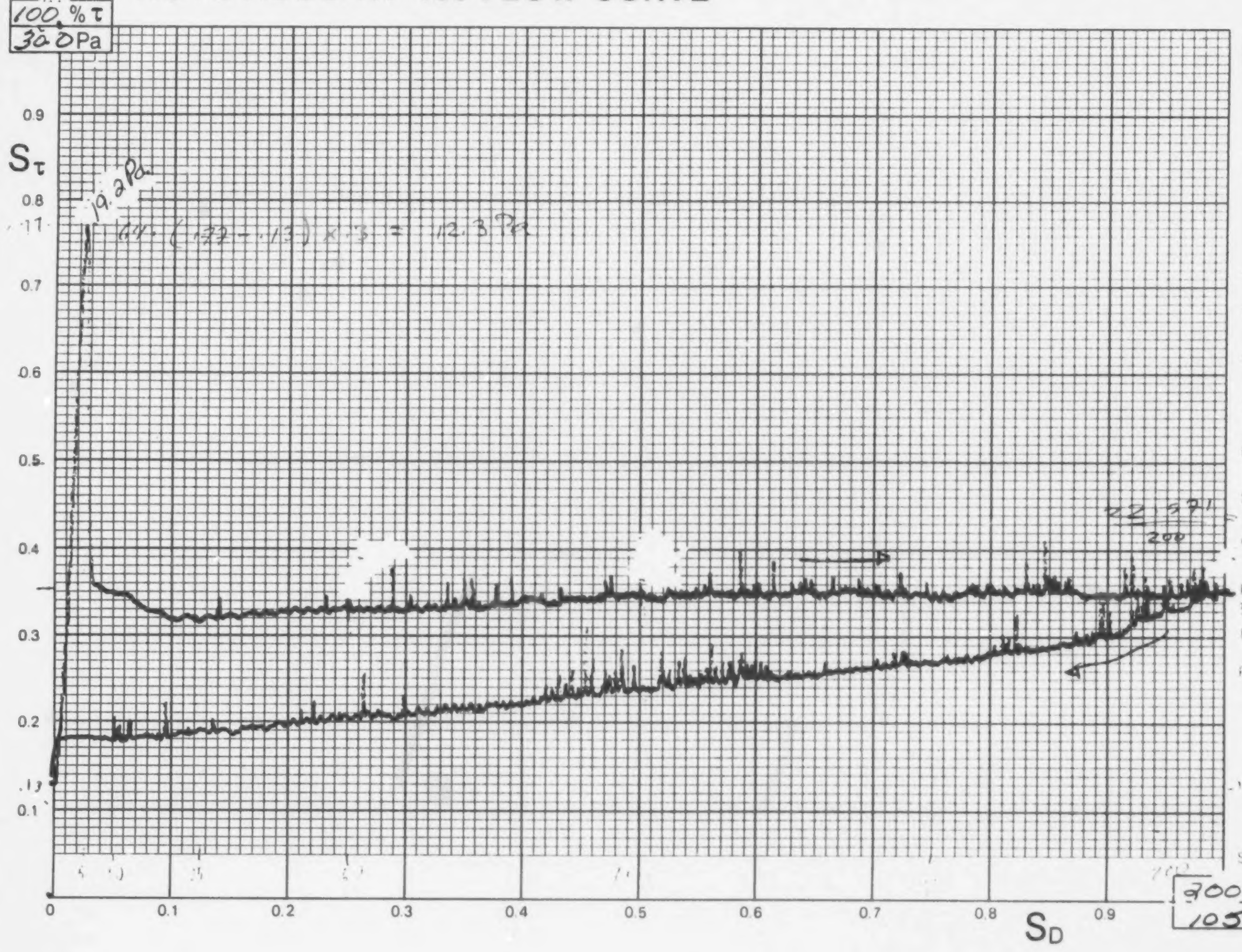
ROTOVISCO RV-100 FLOW CURVE

sit 12.3hr (after 11hr run)



HAAKE

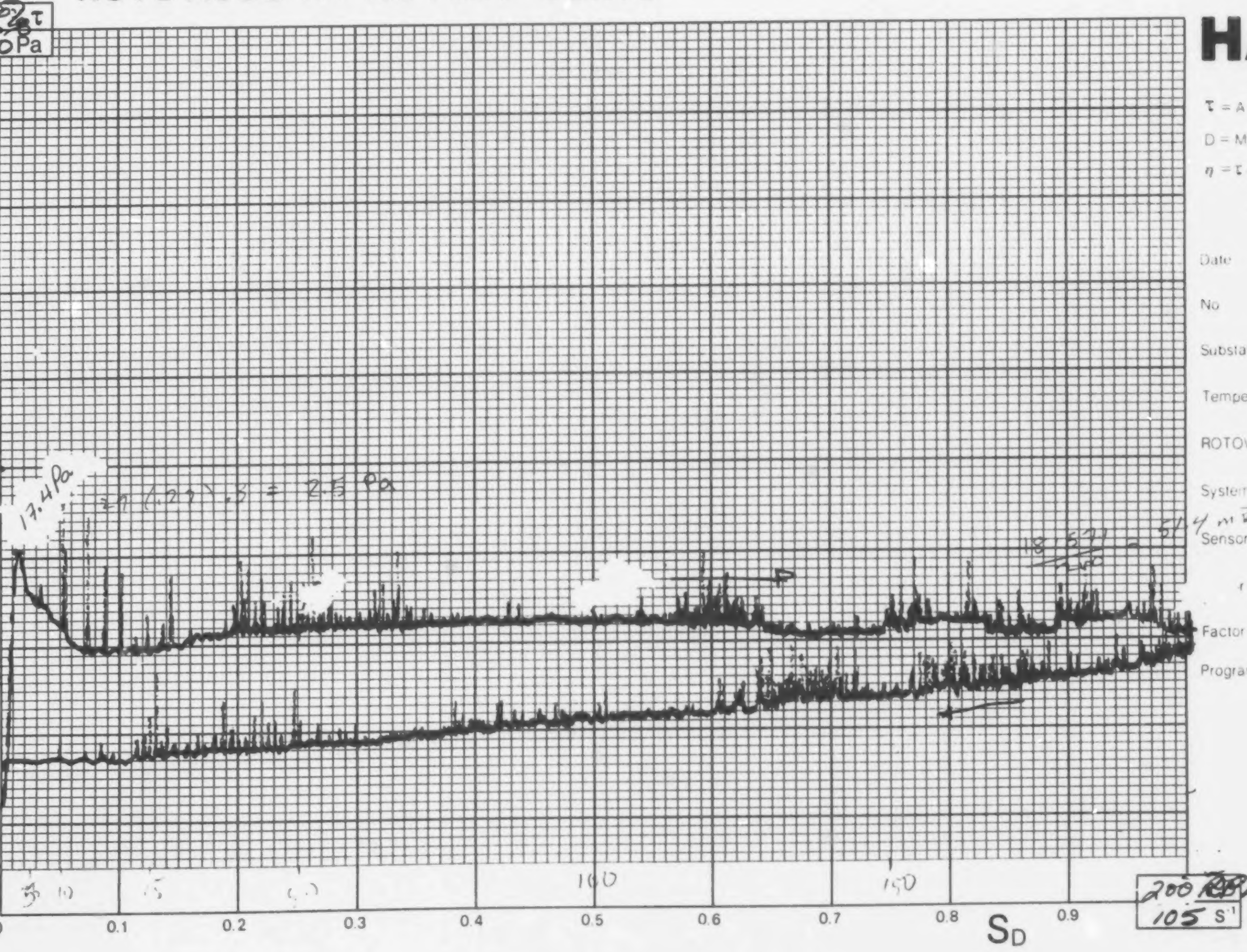
τ = A·%τ·Sτ [Pa]
D = M·%D·S_D [s⁻¹]
η = τ/D [Pa·s]

Date 01/22
No 85
Substance
Temperature
ROTOVISCO RV 3
System MK50
= 62.8 mPa.S
Sensor system MV I
Factor A Pa 0.300
Factor M 0.5255
Program times
T_1
T_2
T_3
Signature

Order No. 10-87-911

HAAKE, INC. • 244 Saddle River Road • P.O. Box 549 • Saddle Brook, N.J. 07662 • (201) 843-2320 sit 25.5hr (after 24h run)

ROTOVISCO RV-100 FLOW CURVE



HAAKE

$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]

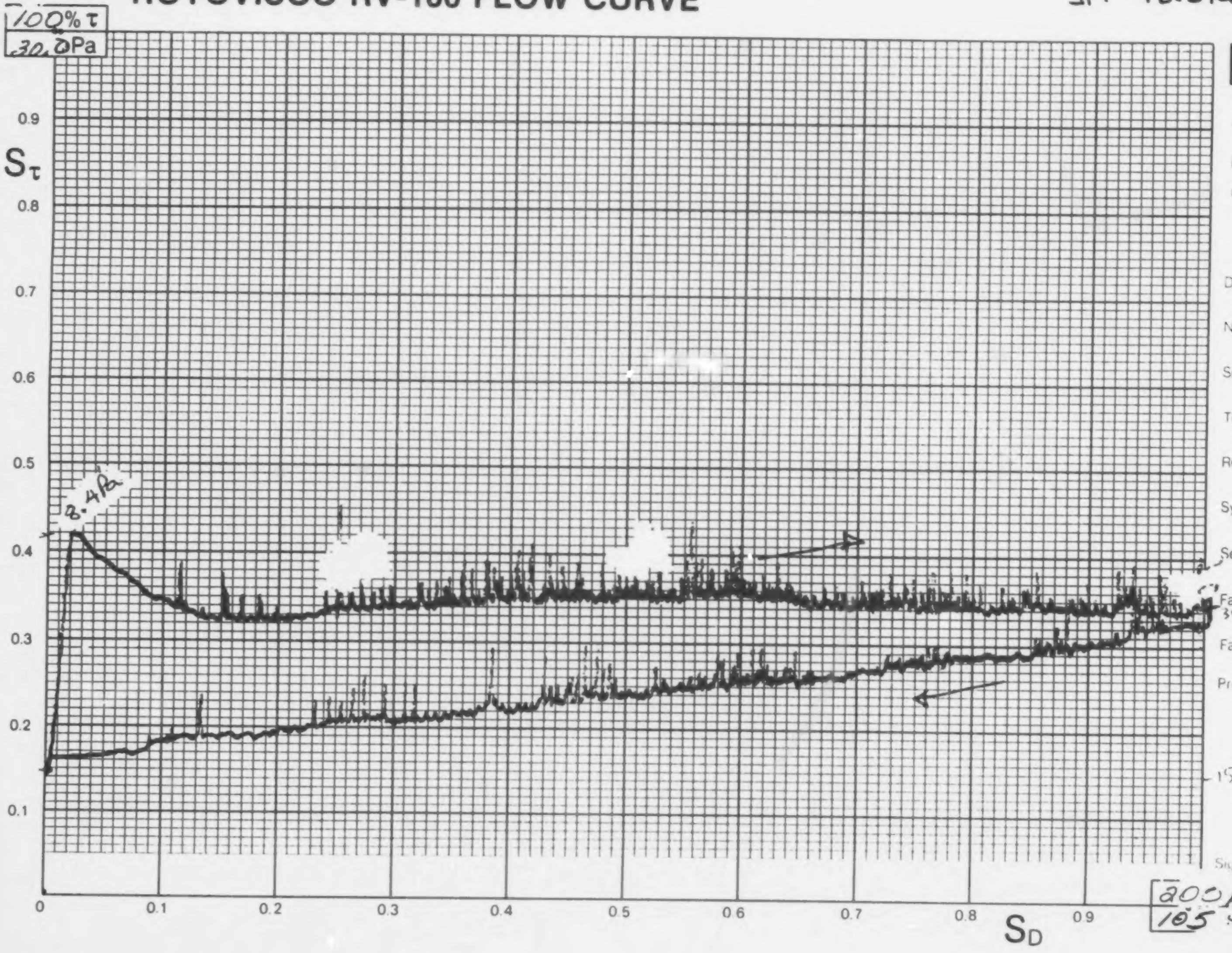
$D = M \cdot \%D \cdot S_D$ [s^{-1}]

$\eta = \tau / D$ [Pa·s]

Date 01/23
No 95
Substance
Temperature 21.1
ROTOVISCO RV 3
System MK50
Sensor system MV I
r A Pa 0.300
Factor M 0.5255
Program times
T₁
T₂
T₃
ie

ROTOVISCO RV-100 FLOW CURVE

sit 46.5hr (after 48hr run)



HAAKE

$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]

$D = M \cdot \%D \cdot S_D$ [s^{-1}]

$\eta = \tau / D$ [Pa·s]

Date	01/26
No	1: 105
Substance	
Temperature	22°C
ROTOVISCO RV	3
System	MK50
Sensor system	MV I
Factor A	0.300
Factor M	0.5 155
Program times	
T_1	
T_2	
T_3	
Signature	

Order No 10 87 911

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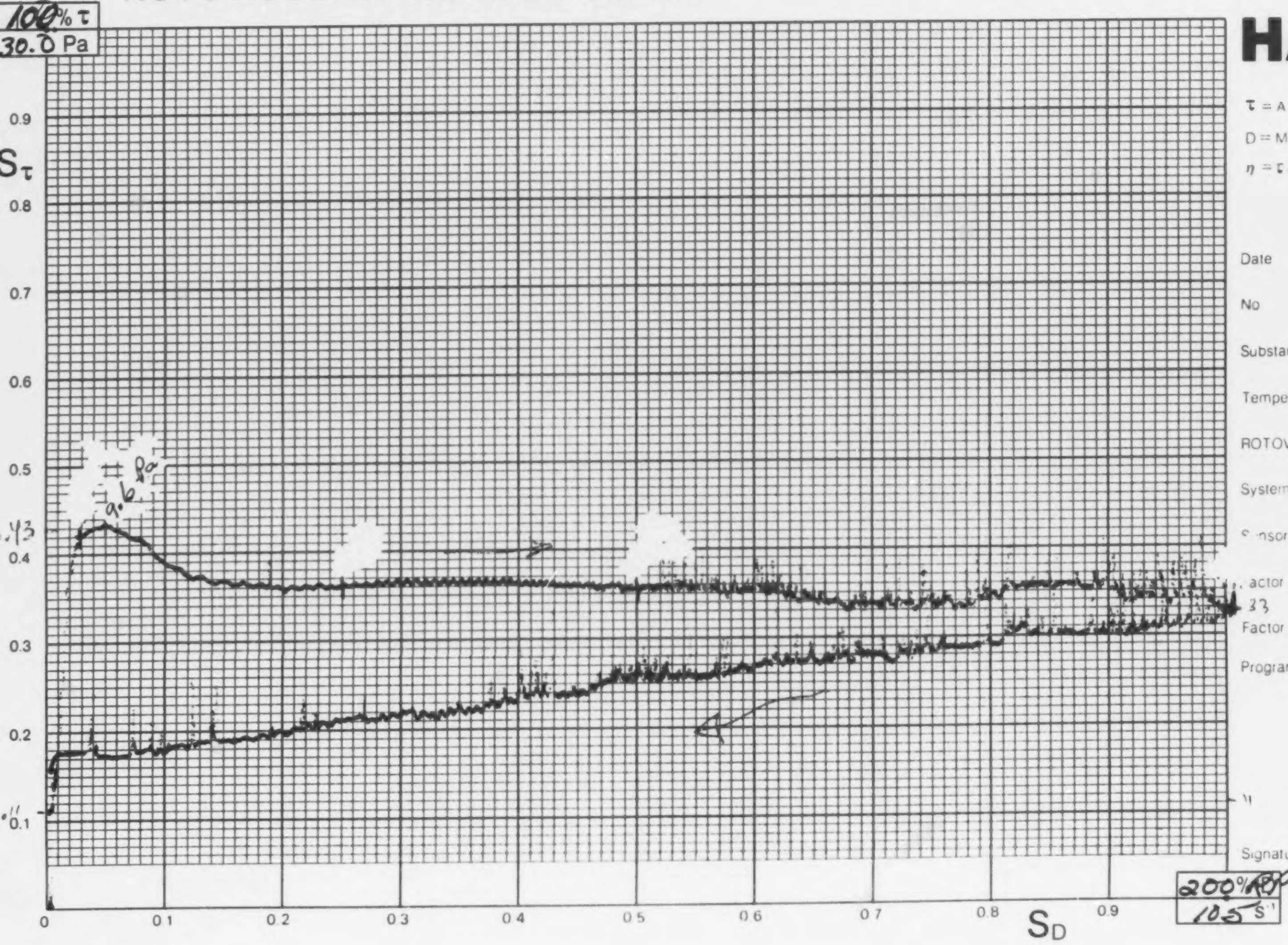
RV 847A 1e

ROTOVISCO RV-100 FLOW CURVE

sit 96hr (after 96hr run)



HAAKE

$\tau = A \cdot \%\tau \cdot S_\tau$ [Pa]

$D = M \cdot \%D \cdot S_D$ [s^{-1}]

$\eta = \tau : D$ [Pa·s]

Date 01/29

No 115

Substance

Temperature 20.7

ROTOVISCO RV 3

System MK50

Sensor system MV I

Factor A Pa 0.300

Factor M 0.5255

Program times

T1

T2

T3

Signature

VOLUME II

VOLUME II

LONG TERM SETTLING

Rob Schutte

Syncrude Canada Ltd., Research,
Edmonton, Alberta

and

Kathy Pongar

Alberta Research Council
Oil Sands and Hydrocarbon Recovery Department
Edmonton, Alberta

March, 1990

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- 2.2.2 Settling of Reconstituted and Diluted Sludge 2
- 2.2.3 Conclusions and Recommendations 7

2.3 SETTLING OF CLEANED SOLIDS 7

- 2.3.1 Conclusions and Recommendations 10

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LIST OF FIGURES

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FIGURE 2: Settling of 2M Column

FIGURE 3: Settling of 2M Column

FIGURE 4: Comparision of Various Sludge Cylinders Equating Time Feb 11/87 as Zero

FIGURE 5: Comparison of 100% Cleaned Solids

2.1 LONG TERM SETTLING

The property of sludge that makes it an industrial and environmental problem is its slow settling rate. A large volume of sludge such as the 10m by 1m sludge sample at the University of Alberta Civil Engineering Department typically settles less than 3% per year.

Settling in this context means a reduction in volume of the sludge layer. It does not mean free settling as expressed by Stokes Law. Nor is it meant in the geotechnical connotation of more or less freely moving particles which can and do slip past each other.

A geotechnical term which is often used in connection with the slow volume reduction of sludge is "consolidation". However the classical mechanism of consolidation is the movement of water from a soil under an applied stress. A large part of the volume reduction of sludge may be due to a (slow) rearrangement of particles in aggregates (ref 1). The driving force for this rearrangement does not have to be an applied stress or gravity. Consolidation therefore would not be an appropriate term to use.

An appropriate measure of the extent to which sludge is altered by treatment is the change in its settling rate. If it increases due to some processing then one of the causes of the slow settling rate was affected. For this reason settling tests were done routinely and used in a comparative sense. Settling tests were not done to generate data with which to design tailings ponds or field tests for the reason that sample sizes were not adequate for such quantitative applications. To illustrate this point further, as mentioned above large volumes settle about 3% per year. All regular sludge samples in this research program settled over 9% in the first year.

Settling data are not normally included when one thinks of physico-chemical properties. However, in a real sense, settling reflects a sum of complex and highly interactive physical and chemical properties and is one more measure of sludge properties.

Two results based on an analysis of settling data will be presented in this chapter:

- Long term settling of diluted sludges shows that there are structural units in sludge that are not broken up by dilution with mild agitation.

- Settling data on cleaned sludge solids together with an analysis of the water phase show that it is possible to affect settling by subtle changes in the chemistry of the adsorbed layers.

2.2 LONG TERM SETTLING AFTER DILUTION

2.2.1 Settling in a Tall Cylinder

A 2m tall by 49 mm ID glass tube was manufactured at the glassshop of the Chemistry Department of the University of Alberta. It was rinsed with distilled water to ensure that the walls were waterwet and sludge was poured in while the tube was held under a 30° angle from vertical to ensure that the sample would run down the wall and not splash or trap air. The sample was then installed against an inner wall in the sample bank storage area of the Clover Bar facility of the Research Council of Alberta. This room is normally dark so that algae growth is not a problem.

Sludge height was measured frequently (when compared to settling rate). The data are given in Figures 1 to 3. Figure 1 illustrates that after an initial slow settling period of about 1700 hrs the rate picked up and stayed high for 1300 hrs. It then slowed down over 1000 hrs to a constant rate for the next 5000 hrs, after which the rate slowly decreased.

The constant rate portion of the settling curve can be extrapolated back to where the line intersects the original sludge height of 199.2 cm. Intersection occurs at -1600 hrs. This is within a few days of the time when the sludge was sampled at Syncrude Research and transferred to 5 gallon pails. These pails were later transported to the Alberta Research Council where a subsample was taken after the then supernatant water was gently stirred back into the sludge. The implication is that the sludge contracted linearly from the pail-fill time onward and that the speed-up of settling between 1700 and 3000 hrs is nothing more than free water reaching the top of the column. This free water was stirred into the sludge by virtue of the gentle stirring that was done on the contents of the five gallon pail.

If sludge was a dispersion of fine particles that repel each other then one would expect that upon dilution the particles would immediately move apart and the rate of subsequent volume reductions would be declining monotonously. The observed variability in settling rate is best explained by the presence of pockets of more or less free water, that is free of suspended solids. However free water cannot exist within a dispersion of mineral particles kept apart by repulsive forces. Thus leading inevitably to the hypothesis that the mineral particles are subject to attractive forces as well as to repulsive forces.

2.2.2 Settling of Reconstituted and Diluted Sludge

Experiments that confirm the conclusion that sludge seems to have a "memory" for its volume are illustrated in Figure 4. Each sludge in this figure is related back to its pre-dilution volume as 100%. Thus 60 volumes sludge diluted with 40 volumes water has a volume of (40+60)/60=166 vol%. After the first five experiments were underway for about a year, a new settling experiment was started (#142) with the same sludge from the same pail and again after gentle stirring. After only 4000 hrs this sludge had settled as much as the sludge that was started almost a year earlier. A repeat of this experiment 1300 hrs later showed the same phenomenon (exp 204 and 205 Figure 4). Supernatant water was removed from the top of the pail, the underlying sludge was sampled into settling cylinder #204 and the appropriate amount of supernatant was stirred back into the remaining sludge in the pail, from which sample #205 was taken.

FIGURE 1

SETTLING OF 2M COLUMN

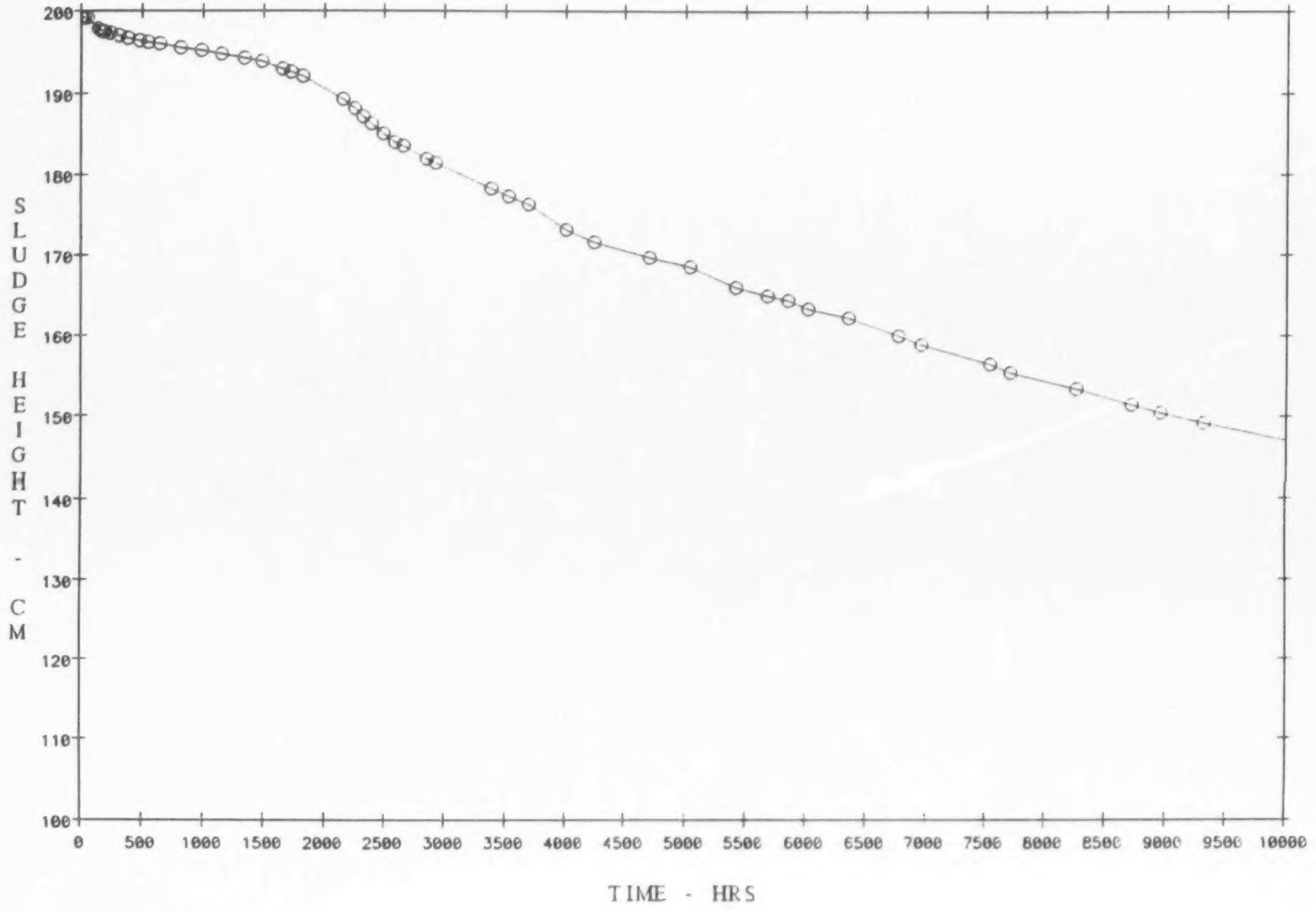


FIGURE 2
SETTLING OF 2M COLUMN

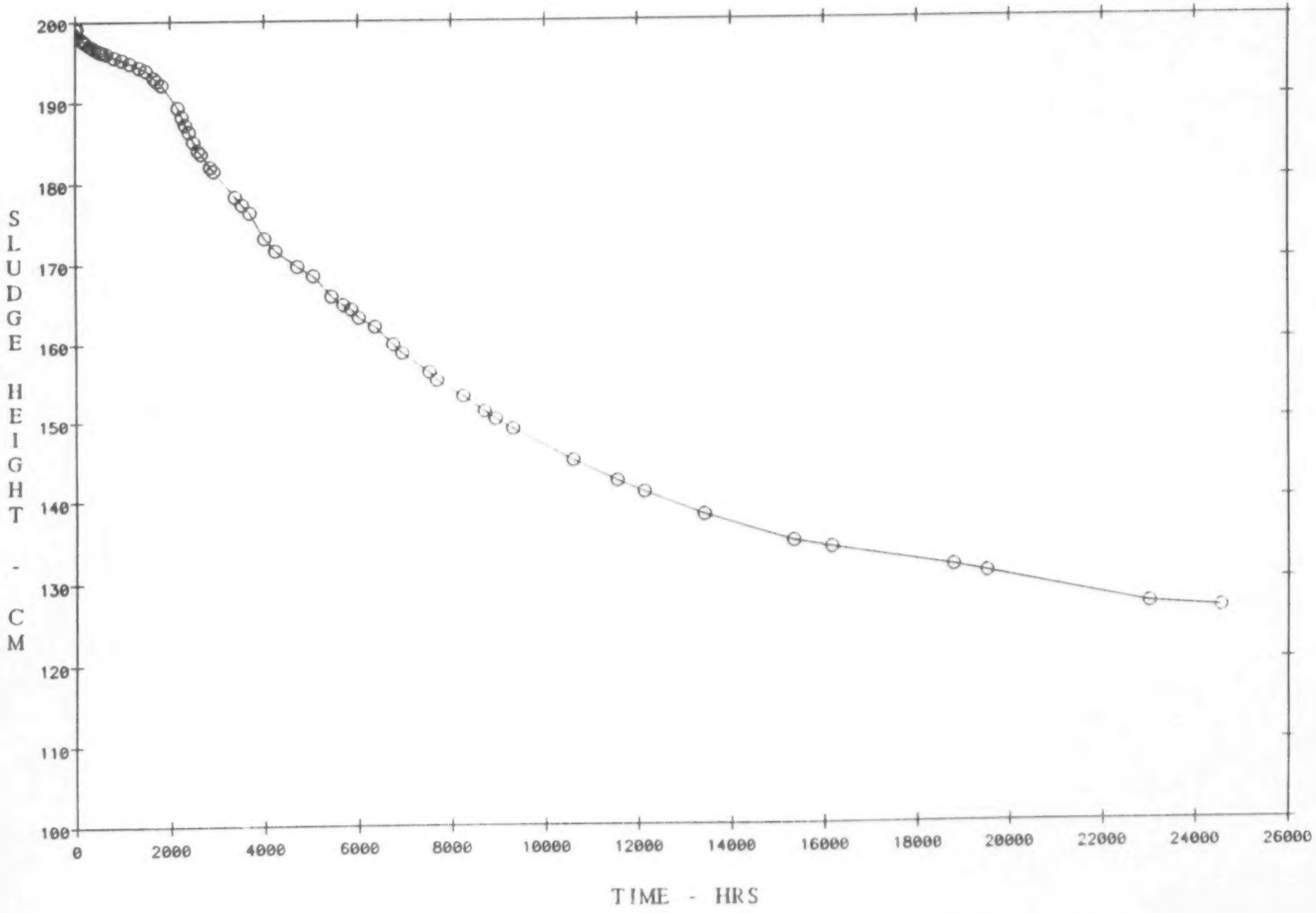


FIGURE 3

SETTLING OF 2M COLUMN

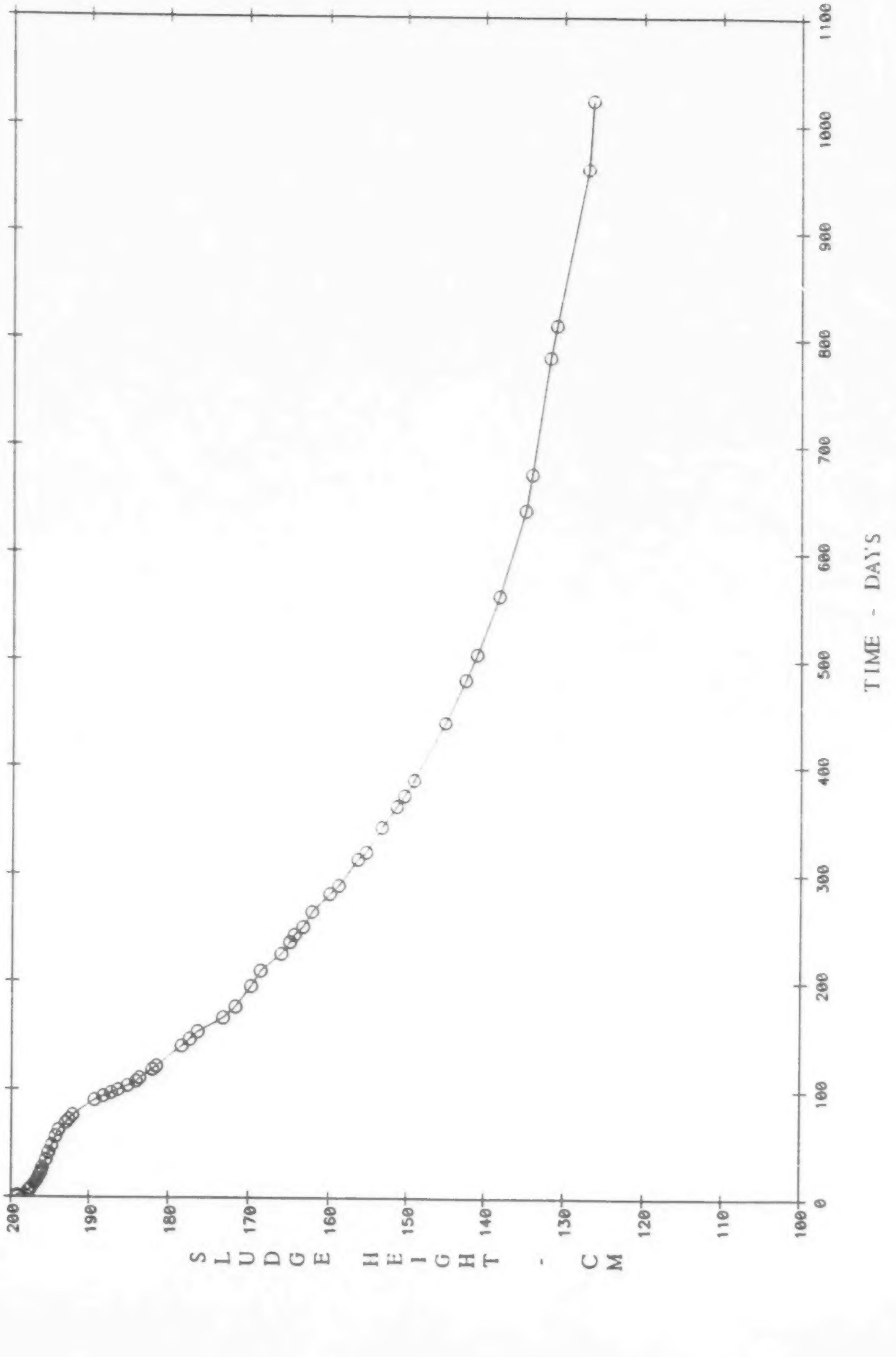
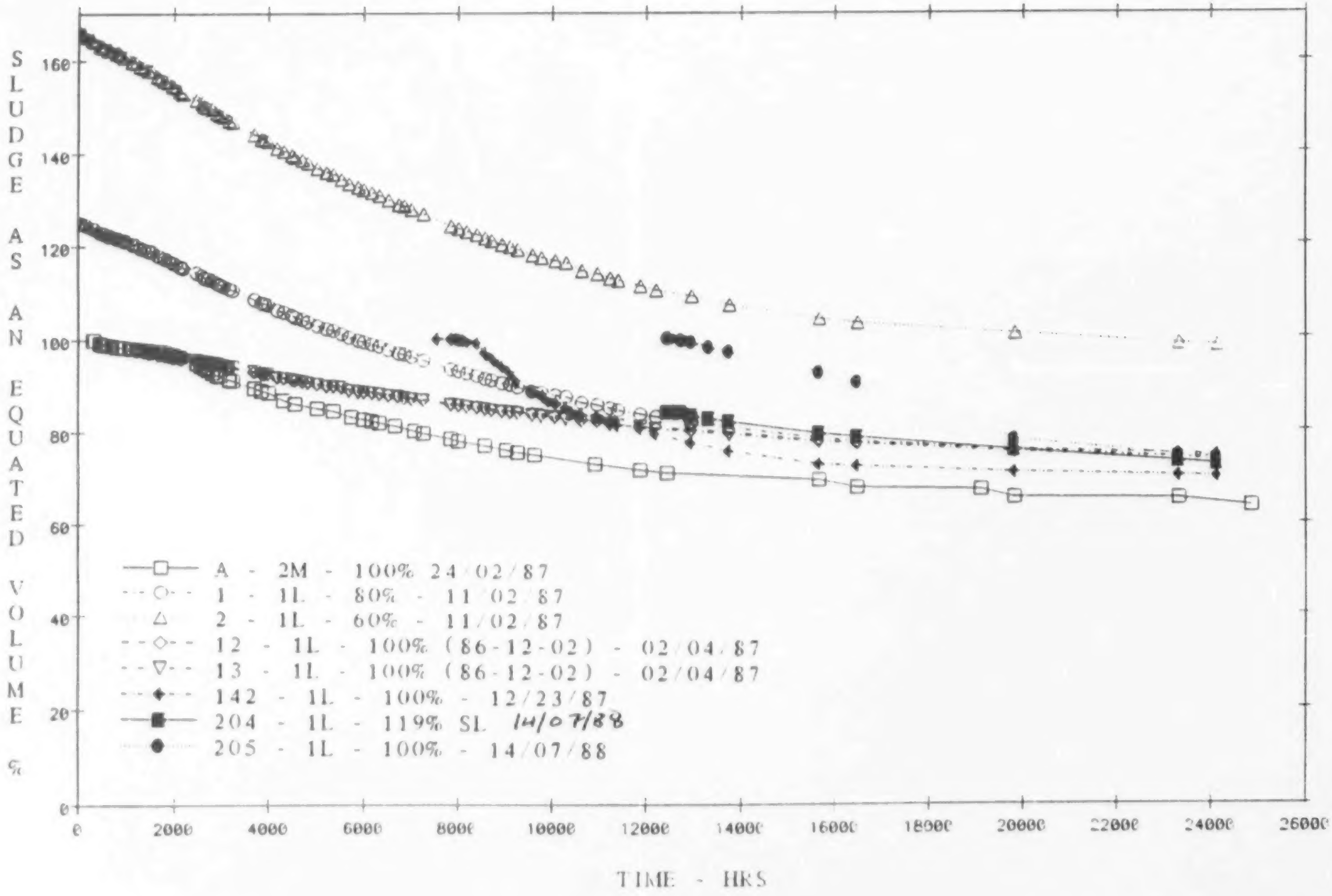


FIGURE 4

COMPARISON OF VARIOUS SLUDGE CYLINDERS
EQUATING TIME TO FEB 11/87 AS ZERO



2.2.3 Conclusions and Recommendations

These experiments show that care must be taken when sampling sludge with the purpose of determining settling or consolidation rates. It is almost inevitable that the rates measured are too high as the sample has previously undergone some settling.

The experiments with dilution show that the concentration of aggregates in sludge can be reduced by dilution but the size and the shape of the aggregates does not change.

It is important that studies of sludge properties as a function of solids content (e.g. freeze-thaw) are not done with artificially densified or diluted sludges but with natural sludges of differing solids content.

2.3 SETTLING OF CLEANED SOLIDS

To obtain a measure of the importance of bitumen and bitumen derived compounds on settling characteristics, a set of sludge mineral solids was prepared by sequential extraction of the hydrocarbons and polar components. Synthetic sludges were then made up with the same solids content as the parent sludge (27 wt% solids) and with water that was obtained from the parent sludge through centrifugation.

Results are illustrated in Figure 5. It can be seen that extracting hydrocarbons and mildly polar components with Toluene/isopropyl alcohol (IPA) mixtures (yielding solids I) led to roughly a doubling of the settling rate. In 3800 hours the sludge had settled to 74% of original volume. This compares to 88.5% for the 2m sludge (Figure 1).

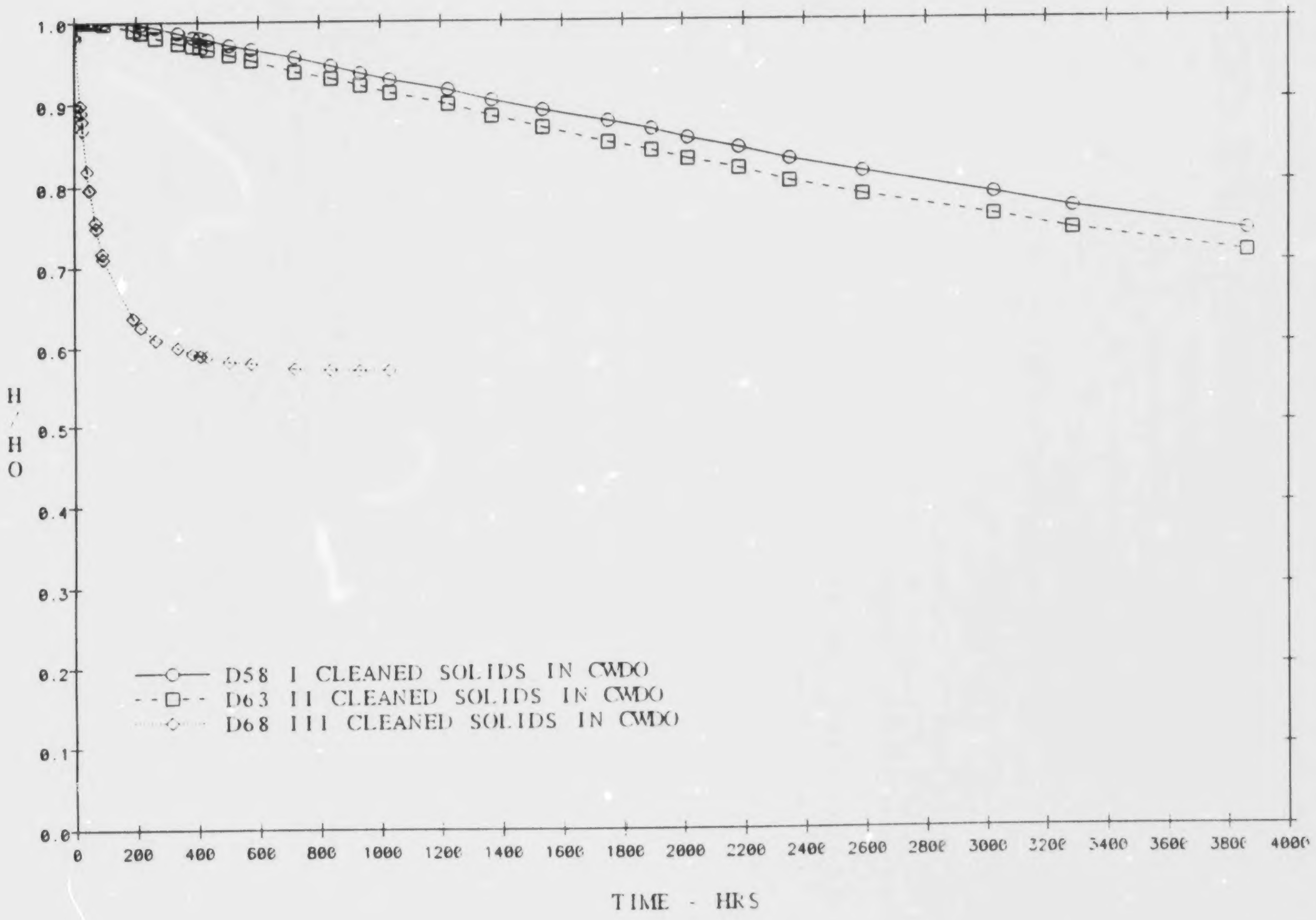
Washing solids I with methylene dichloride (yielding solids II) did not materially improve settling but washing solids II with methanol (yielding solids III) had a dramatic effect on settling. Within 50 hours the 80% mark was passed and in 400 hours the sludge had settled to 59% of its starting volume.

The latter result is significantly different from the starting sludge. This does not necessarily mean that the slow settling of sludge is caused by the presence of organics on the solids. Several factors changed while cleaning the solids. Ultrafine (<100 nm) particles were definitely lost with the decant operation on the solvents after centrifugation of solids/solvent mixes. These fines have significant Brownian motion and are not easily centrifuged down from the wash liquid. Most of these particles that were washed out were lost with the Toluene/IPA wash. Ultrafines should be considered as well as bitumen when explaining the higher settling rates of solids I and II as compared to the parent sludge.

An explanation for the fast settling rate of the methanol washed solids (solids III) may be found in the accompanying change in the water chemistry. Cleaned solids were extracted with deionized water and the soluble solids were analysed. A surprise finding was that for solids III the calcium concentration was an order of magnitude higher than for solids I or II. See Table 1 for a complete listing of the major cations. Not much change was observed for sodium or potassium.

FIGURE 5

COMPARISON OF 100% CLEANED SOLIDS



COMPOSITION OF SUPERNATANT WATER

FROM SLUDGES MADE WITH CLEANED SOLIDS

EXPERIMENT NO.	—·—	43	48	53	68	120
SOLIDS	SL 1]	I	II	III	III	III
WATER Phase 2]		dH$_2$0	dH$_2$0	dH$_2$0	CWDO	dH$_2$0b
Si	4.2	21.0	8.3	19.9	19.4	23.0
Na	455	293	293	341	552	346
K	9.0	15.5	14.5	17.7	11.7	18.9
Ca	6.3	5.9	10.2	75.5	7.3	29.6
Mg	4.3	12.2	13.2	78.0	31.0	84.5
Fe	0.2	1.0	<0.1	<0.1	<0.1	<0.1
Al	<0.2	4.3	<0.2	<0.2	<0.2	<0.2

NOTES: 1] whole parent sludge

2] Water used to make up 27wt% sludge
dH_2O = deionised water
CWDO = sludgewater (centrifuged and deoiled)
dH$_2$0b = deionised water; sludge was boiled for 10 min.

It is not clear why contacting solids II with methanol would render calcium and magnesium extractable from the solids by deionized water. A tentative explanation is that these elements are bound or complexed to humic acids or surfactant acids and that these acids become esterified by methanol thus releasing their original counter ions. This mechanism is compatible with the observation that the organic carbon content of solids II and III is the same (Vol. 1, Table 6).

Qualitatively, the following observations confirm this mechanism also. Solids II are shaken for 1.5 hr with 0.1 N NaOH followed by centrifugation. The supernatant liquid is black from humic materials. The same experiment with solids III yields a red-brown solution. This may indicate that the methanol wash reduced the quantity of base extractable organic (acid) material.

A possible mechanism through which the methanol wash changed the settling rate is than that the released calcium and magnesium compressed the electric double layer around the mineral particles, causing them to flocculate. The unit particles are thus larger and denser than in the parent sludge. Permeability is enhanced and quick settling follows. An alternative theory is that in solids I and II the organic "coating" is a repulsive coating because of the carboxylic acid groups. When these groups are esterified with methanol, their repulsion is eliminated. The organic coatings may actually coalesce and a dense sediment ensues. These theories can be examined through additional experimentation and observation by microscopic techniques.

2.3.1 Conclusions and Recommendations

The changes in water chemistry and in settling rates resulting from methanol treatment point to a connection between multivalent ions and humic materials. Further research should be done to understand how these complexes influence the degree of dispersion and/or the strength of the agglomerates.

Ref: P.J. Crickmore, R. Schutte, J. Causgrove, "Fractal Geometry and The Settling of Oil Sand Tailings Sludge". Proceedings Vol. 1, page 217, 4th Unitar/UNDP International Conference on Heavy Crude and Tar Sands, Edmonton, Alberta 1988.

VOLUME III

VOLUME III

ELECTROKINETIC PROPERTIES OF SOLIDS FROM HOT WATER PROCESSING OF ATHABASCA OIL SAND

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INTRODUCTION

As part of CANMET contract that examined the fundamental properties of tailings from Hot Water processing of Oil Sand (commonly referred to as sludge), the Alberta Research Council, Oil Sands and Hydrocarbon Recovery Department, conducted experiments in determining the electrokinetic properties of the solids in the tailings. Previous investigations have shown that certain chemical modifications of the sludge can result in increased sedimentation rates of the solids (1). It was thought that determining the electrophoretic mobility of these solids could reveal information about the enhanced settling rates.

The electrophoretic mobility of solids from the tailings ponds, both in the original state and those that had been treated with different combinations of solvents, was measured in the presence and absence of pond water over a wide range of solution pH and electrolyte concentration. The results show that in pond water the electrophoretic mobilities for all the solids were the same. In solutions that did not contain pond water, however, there is evidence that some kind of organic compound is present on the surface of the solids from the tailings pond.

EXPERIMENTAL

Preparation of the Solids

The experiments were carried out using a subsample of tailings sludge which was taken from a storage tank from Syncrude's tailings pond in August of 1986. Solids, separated from sludge by centrifugation, were treated with different organic solvents. Solid I was treated with a 50/50 toluene/isopropanol (IPA) mixture. Solid III was obtained further treating solid I with dicholoromethane and then methanol. Details of the exact preparation have been reported elsewhere (1). A high purity kaolinite (Georgia Kaolin Co., New Jersey) was also used.

Zeta Potential Determination

The dispersions for the sludge and the solids were prepared slightly differently. The sludge was diluted approximately 1:500 into the desired solution. For the solids, a few milligrams of material was dispersed using an ultrasonic cleaning bath.

'SLudge water' was water from the centrifugation of sludge taken from the tailings pond that was filtered to remove the visible oil and the small amount of solids. Ion analysis of the sludge water is given in Table 1. In some experiments, the sludge water was diluted with deionized water, or small amounts of a concentrated NaCl solution were added. After the dispersion was prepared, the pH was altered by adding a small amount of concentrated NaOH or HCl. The pH was then monitored for one hour, using a pH meter (Corning model 135) with a combination glass electrode, to insure that it did not change.

Electrophoretic mobilities were determined using a Rank Brothers Electrophoresis Apparatus (Rank Brothers Inc., Cambridge, England). A flat cell equipped with platinum electrodes was used. All measurements were conducted a 30°C. In most experiments, the velocities of 20 particles were

Table 1 The Water Analysis of the Sludge Water

Species	Concentration, mg/l
pH	8.2
total organic carbon	92
total inorganic carbon	209
Fe	0.2
Na	455
K	9
Ca	6.3
Mg	4.3
B	1.9
Cl	116
SO_4	2.4

measured. For higher electrolyte concentrations, the effects of joule heating and low mobilities limited the number of particles that could be timed. For NaCl solutions, the relative standard deviation in the timings was usually less than 10%. Measurements in pond water showed greater relative standard deviations of 13%. Zeta potentials were calculated from measured electrophoretic mobilities using the Smoulchowski equation:

$$\varsigma = \frac{\eta}{\varepsilon} U$$

where ς is the zeta potential, η and ε are the viscosity and permittivity of the continuous phase, respectively, and U is the electrophoretic mobility.

Electrokinetic Sonic Analysis

Electrokinetic sonic analysis (ESA) was performed using a Matec system (Matec Applied Sciences, Hopkinton, MA). The details and advantages of this instrument have been reported previously (2). One of the advantages is that the instrument can perform continuous measurements while adding a titrant to the sample allowing simultaneous potentiometric and conductimetric titrations.

Samples were prepared for this analysis by diluting the original sludge to 1.5 vol% solids (approximately a 1:7 dilution) or by dispersing an appropriate amount of solid into solution. Measurements were then conducted by titrating with either 0.5 M HCl or 1.0 M NaCl.

RESULTS

Zeta Potentials of the Solids in Pond Water

The electrophoretic mobility of the solids from the tailings, solids I and the kaolinite as a function of pH are shown in Figure 1. As the pH of the solution is increased, there was a slight decrease in the zeta potential. Although each one of the solids have had treatment with different combinations of solvent, the electrophoretic mobilities for the solids were similar. The mobility with pH behavior for kaolinite was not expected. Previous studies (3,4) have shown different mobility and pH relationships for kaolinite in solutions with comparable concentrations of Na^+. This suggested that there may have been some interfering agent in the pond water that was altering the mobilities of the solids.

Measurements were also conducted as a function of solution pH for the sludge particles in pond water that had been diluted 1:1 (vol/vol) with distilled water (leaving an Na^+ concentration of 0.01 M) and in solutions where additional NaCl was added to bring the final concentration of Na^+ to 0.06 M. The results are shown in Figure 2a. Once again very similar mobilities were observed in both electrolyte concentrations.

Similar measurements were conducted using solids I. In this case, however, the pond water was diluted 1:20 with distilled water for a Na^+ concentration of 0.001 M. Measurements were also performed by adding additional NaCl to bring the concentration to 0.06 M. The results are shown in Figure 2b. In 0.001 M Na^+, the mobilities at pH values greater than 7.0 are slightly more negative than for the higher Na^+ concentration. Whether this is due to the effect of expanding the double layer because of decreased electrolyte concentration or because of the dilution of the interfering agent present cannot be determined from these data.

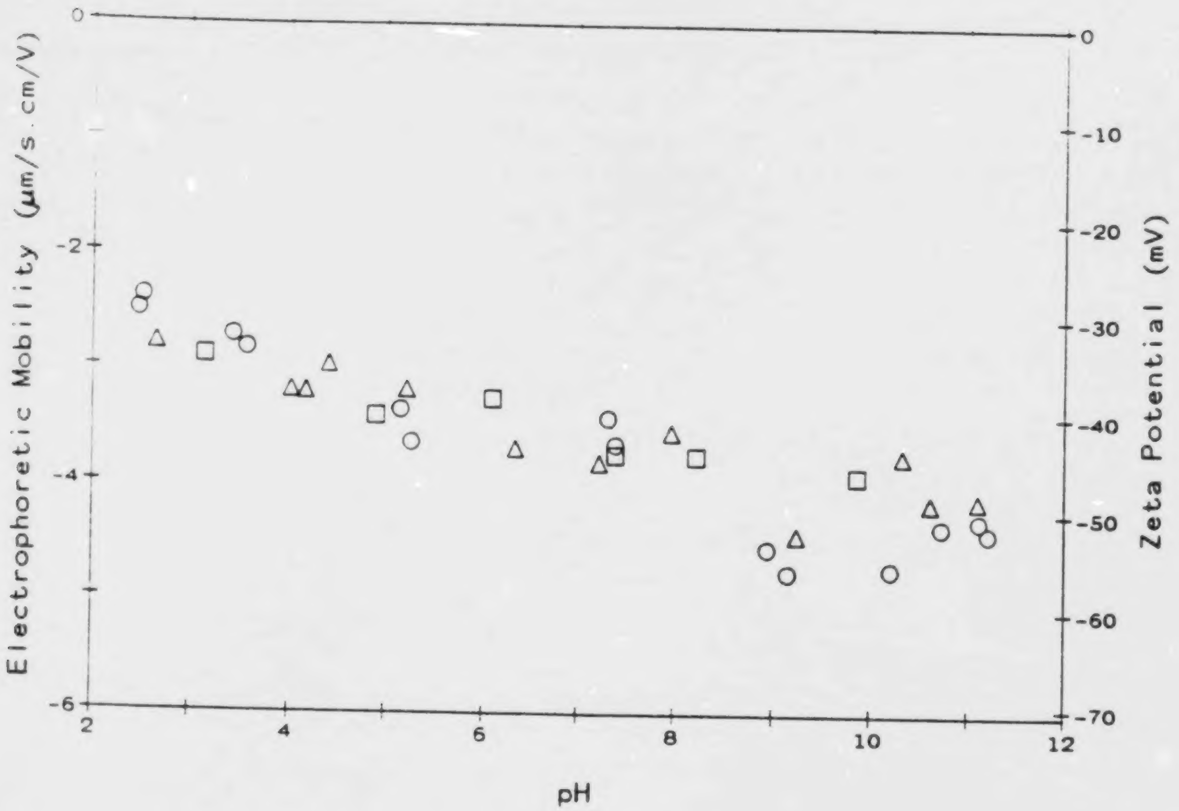

Figure 1. Zeta Potential as a Function of pH for Tailings Sludge (○), Solid I (△), and Kaolinite (□) in pond water. The zeta potentials are the same. The zeta potentials for kaolinite were expected to be different than what was observed. Therefore, some surface active agent in the pond water is influencing the zeta potential.

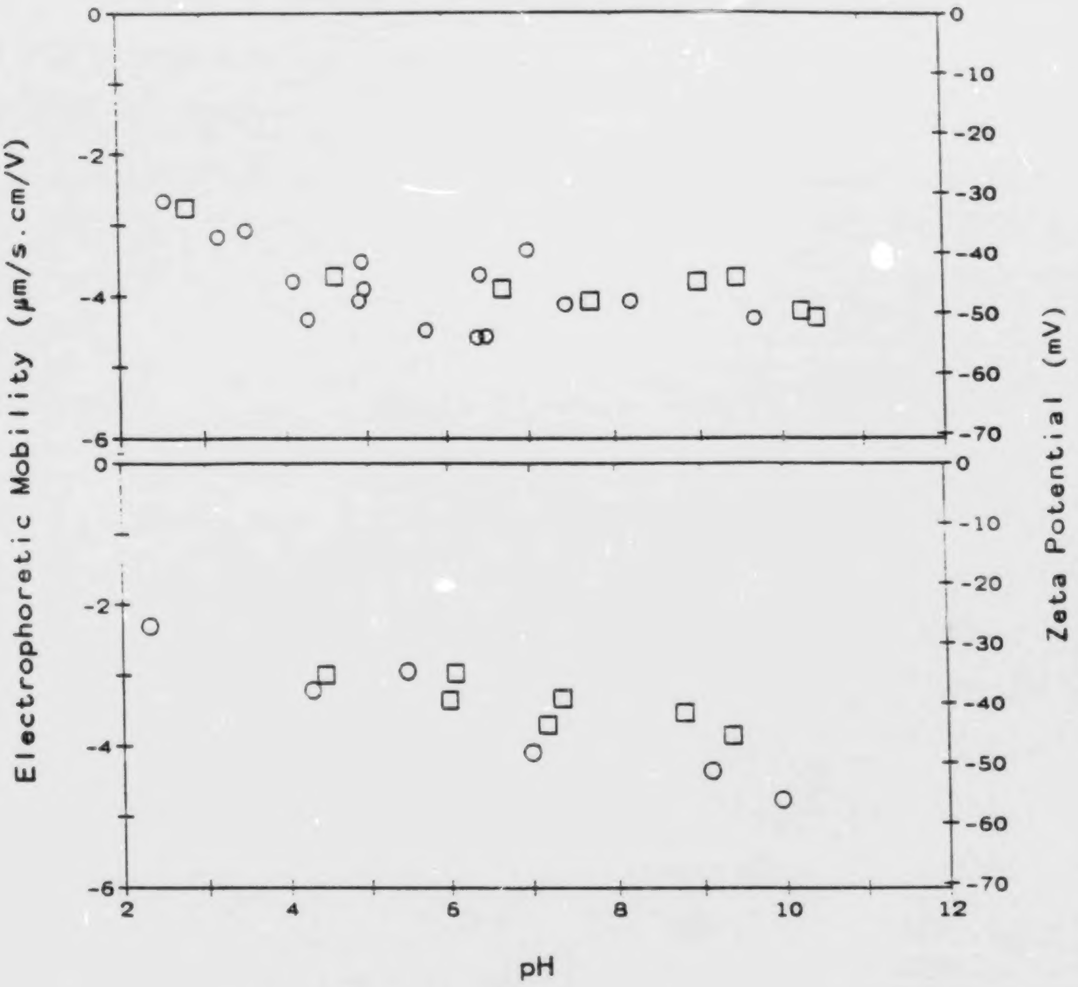

Figure 2(a). Zeta potential as a function of pH for Tailing Sludge in pond water at 0.01 M NaCl (□), and 0.06 M NaCl (○). The zeta potential for the two electrolyte concentrations are similar which suggests that the pond water contains some surface active agent that influences the zeta potential of the particles.

2(b). Zeta potential as a function of pH for Solid I in 0.001 M NaCl (○), and 0.06 M NaCl (□).

Zeta Potentials of the Solids in Solutions of NaCl

In order to investigate the electrophoretic mobilities of the solids without the effects of pond water, measurements were conducted in solution containing NaCl only. Figure 3 shows the electrophoretic mobilities for solids I and kaolinite as a function of pH in a solution containing 0.001 M NaCl. The electrophoretic mobilities of solids I changed very little with respect to what was observed in the diluted pond water (Figure 2b). The mobilities for the kaolinite, however, are significantly different. At solution pH values less than 6.0, the zeta potentials for kaolinite in the absence of pond water were less electronegative. For pH values greater than 6.0, the electrophoretic mobilities for both solids were similar.

To investigate the difference between the mobilities further, mobilities for kaolinite, solids I, solids from tailings, and solids III were measured as a function of solution pH in the presence of 0.02 M NaCl. The results are shown in Figure 4. The mobilities for the solids obtained from the tailings were similar to each other. This was not expected as the the treatment of each solid was significantly different. The kaolinite, however, now exhibited similar behavior as what is found in the literature (3,5).

Electrokinetic Sonic Analysis

Measurements using the ESA were of one of two types; the ESA signal as a function of pH or increasing NaCl concentration. Although it is difficult to compare the magnitude of the mobility determined from conventional electrophoresis with the ESA signal, the behavior as a function of pH should be similar. The measured ESA signals for sludge, solids II, and solids III as a function of solution pH are shown in Figure 5. The signal increases very slowly with increasing solution pH until a value of 6, then levels to a relatively constant value. This was the observed behavior for the zeta

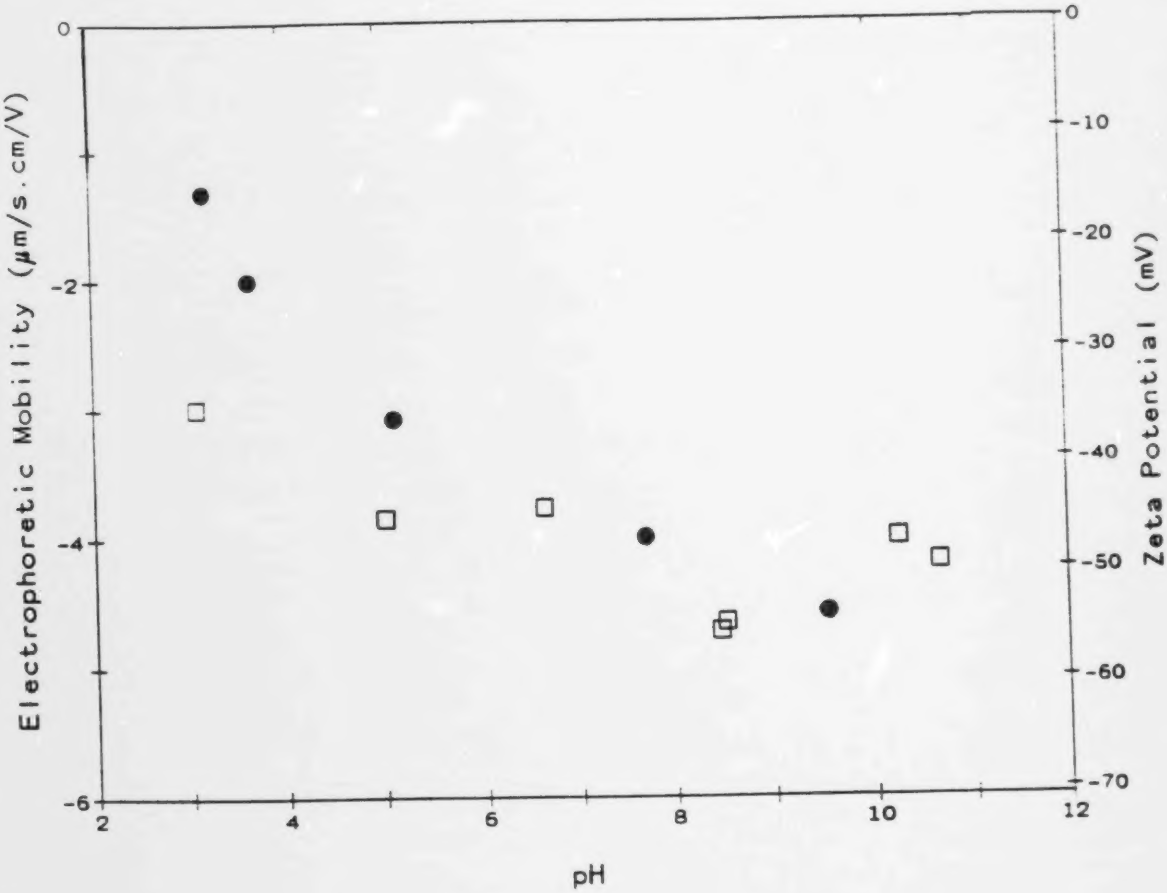

Figure 3. Zeta Potential as a Function of pH for Kaolinite (○) and Solid I (□) in 0.001 NaCl. The curve for kaolinite agrees with values from the literature but the zeta potential of Solid I is more negative at low pH. This shows that there may be surface active agents adsorbed to the surface.

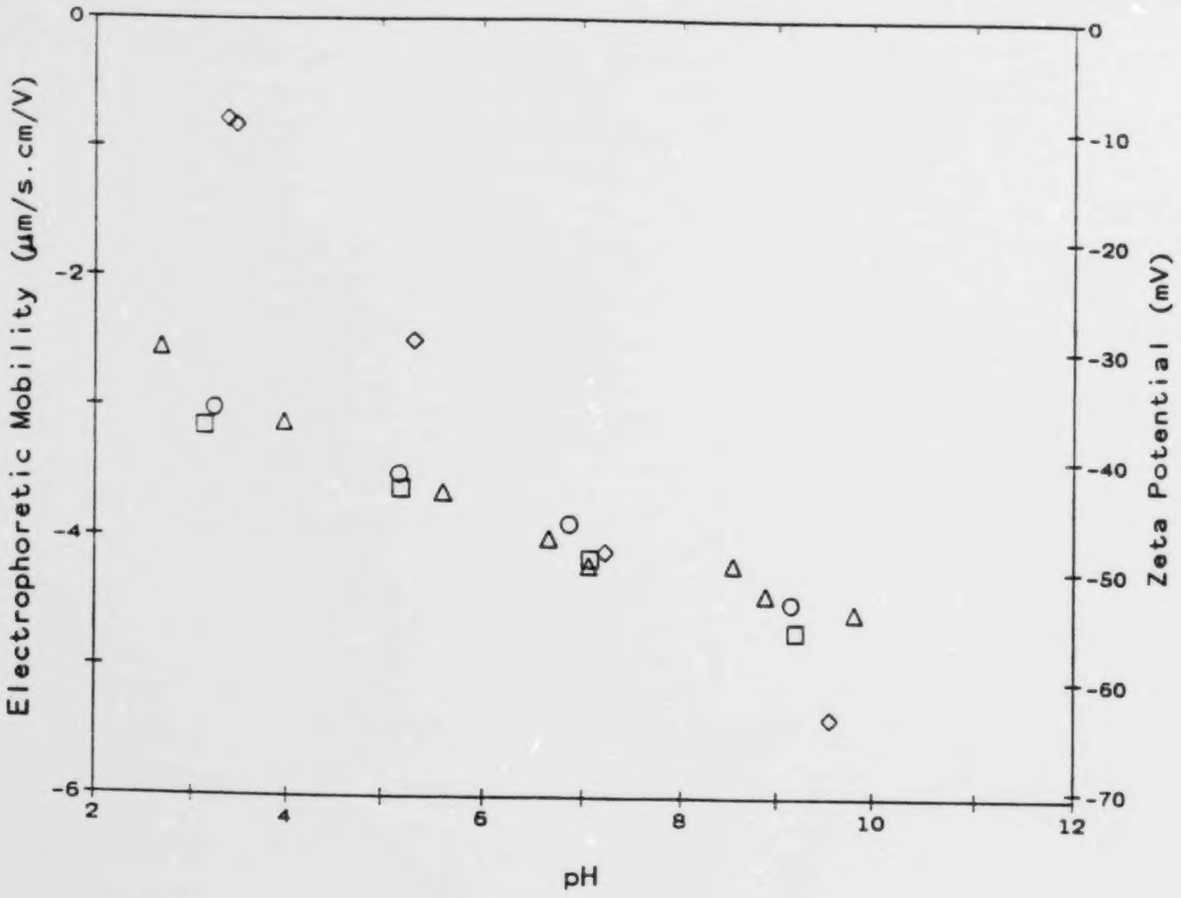

Figure 4. Zeta potential as a function of pH for Tailings Sludge (○), Solid I (△), Solid III (□), and Kaolinite (◇) in 0.02 M NaCl. The zeta potentials for kaolinite are in agreement with what is reported in the literature (11). The zeta potential for the solids, however, are all the same. See text for explanation.

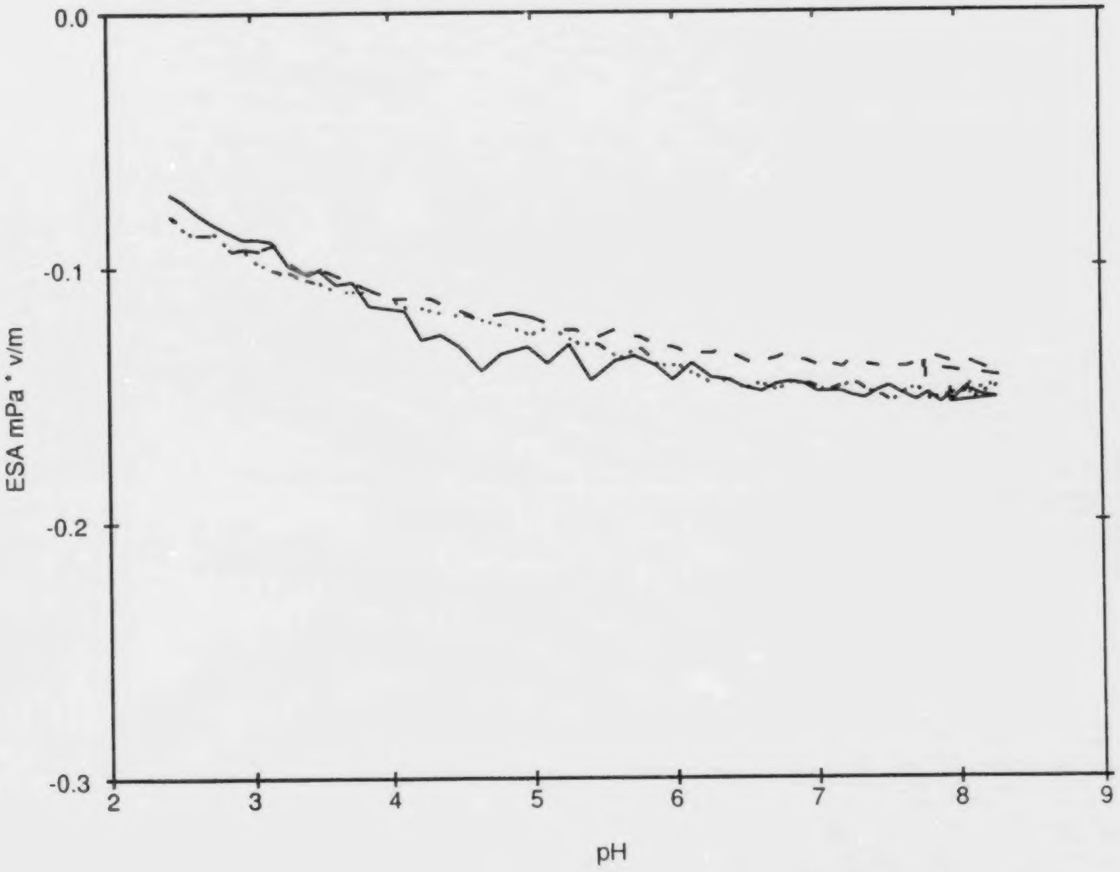

Figure 5 Variation in ESA signal with solution pH. Shown here for sludge (—), solids II (–), and solids III (···). The curve for each solid is very similar.

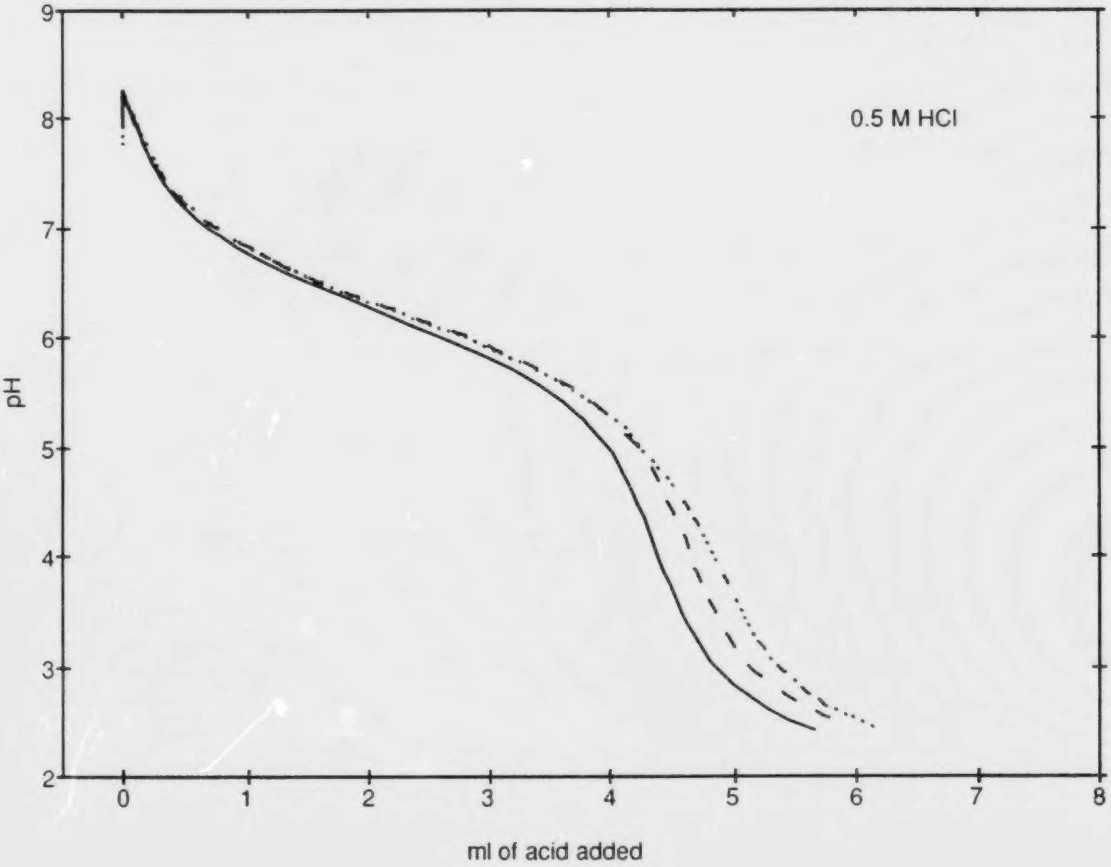

Figure 6 Potentiometric titration curves for the sludge (—), solids II (---), and solids III (•••). The titration curve indicates that the surface is carboxylate in nature and the shift in the equivalence point suggests there is a slight difference in the number of surface groups between the different solids.

potential as a function of pH as determined from conventional electrophoresis (Figure 1).

One of the advantages of the ESA is that potentiometric and conductimetric titrations are performed simultaneously. The results of the potentiometric titrations are shown in Figure 6. The curve divides into three zones, there is an initial sharp decrease in pH that is followed by an area where the pH remains relatively constant, this is followed by another sharp decrease in solution pH. The behaviors can be explained by the following, in the first zone excess base is neutralized, the second zone is due to the neutralization of the surface groups (i.e. the solid surface is acting like a buffer), and the third zone is the addition of excess acid to the solution. The pH at which the 'equivalence point' is reached is approximately 4.0. This corresponds to what would be expected for a carboxylate functional group and indicates that this may be the nature of the interfering agents that adsorb. The second zone can be used as an indicator for the number of groups on the surface. The number of ml of acid to reach the equivalence point for each one of the solids is given in Table 2. There is an increase in the amount of acid required to reach the equivalence point for solids from sludge, solids II and solids III, indicating that the as the severity of the solvent treatment increases, the buffering capacity of the surface increases. This suggests that the that the interferring agent is complexing surface groups and the removal of this agent releases the group to participate in the titration.

Experiments were conducted where the solids were titrated using 1.0 M NaCl. An example of the curves generated in these experiments is shown in Figure 7. The ESA signal slowly approaches zero with increasing NaCl concentration until the signal sharply changes from negative to positive. This will

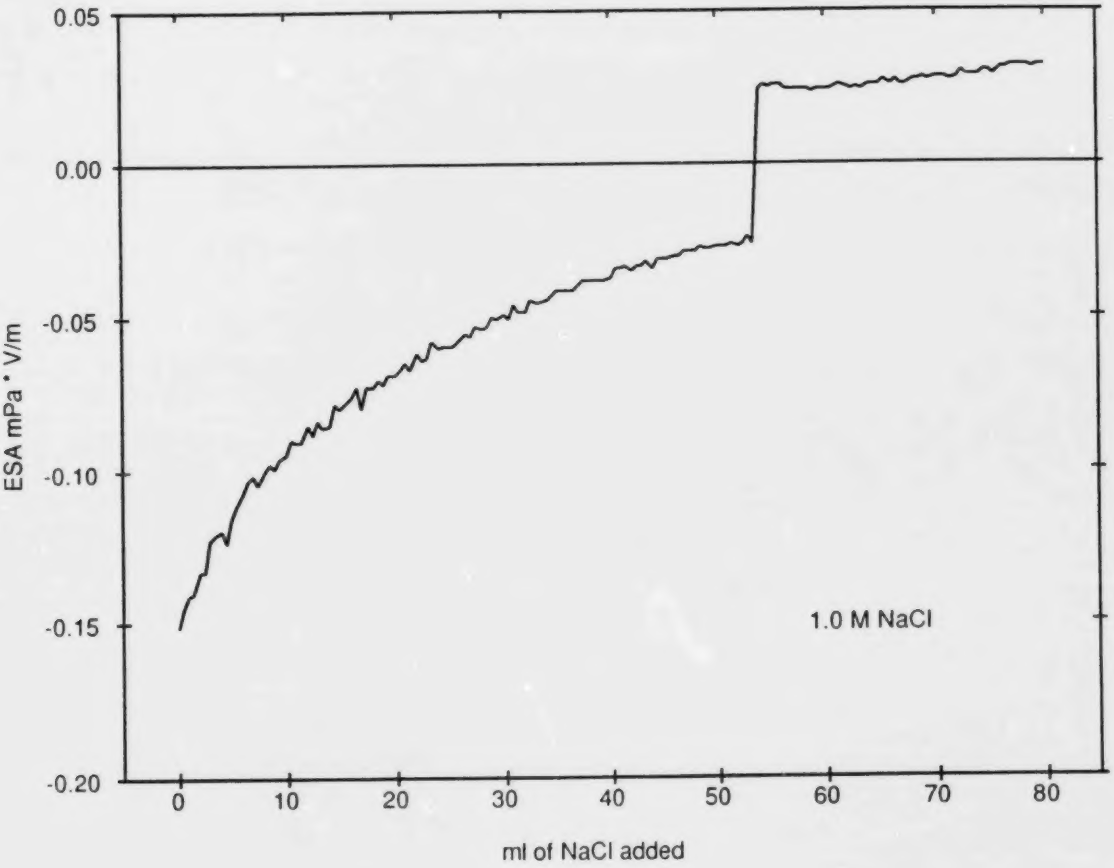

Figure 7 The variation in ESA signal with increasing NaCl concentration for sludge. Curves for the other solids were similar. At a certain concentration of NaCl the signal suddenly changes from negative to positive, presumably due to destabilization of the solids.

be termed the crossover point. Although the reason for this is not known, it is likely due to destabilization of the sludge. The number of ml of NaCl required to reach the crossover for solids from sludge, solids II and solids III is given in Table 2. As the solvent treatment becomes more severe, less NaCl is required to create the crossover of the ESA signal. This seems contradictory to the findings of the potentiometric titration (i.e. more acid was required as the solvent treatment was increased), but it is difficult to compare the two phenomena. The potentiometric titration gives information about the nature and magnitude of the surface charge, while the crossover point of the ESA signal tells us about the destabilization of the sludge. The relationship between surface charge density and dispersion stability is not straightforward (especially with systems like clays where ion adsorption and exchange can occur). More experiments with the ESA are required before a conclusion can be reached.

Table 2 Titration Data From the ESA

Solid Type	ml of 0.5 M HCl to reach equivalence point	ml 1.0 M NaCl to reach crossover point
sludge	4.3	54
solids II	4.7	43,45.8
solids III	4.8	37.5

DISCUSSIONS

The Influence of Adsorption of Surfactants on the Zeta Potential

The results of the electrophoretic mobility measurements showed that there was some interfering agent in the pond water that could influence the mobility of the kaolinite particles and that even though the particles from sludge underwent different treatments with organic solvents, the electrophoretic mobilities were similar. The observations can be explained by adsorption of surfactant on the solid surfaces. During the Clark hot water process it has been shown (6) that natural surfactants are produced and fall into mainly two functional types, carboxylate and sulfonate. The potentiometric titration data showed that the surfactant adsorbed is likely carboxylate in nature. At the pH of the Hot Water Process (>pH 8) it would be expected that both of these would be fully ionized, each possessing a negative charge. For a surfactant to adsorb onto a surface of like charge, either a physical force (eg van der Waals) or a chemical adsorption must take place (7). One of these would be the expected mechanism of surfactant adsorption from the pond water onto the surface of the particles. Of the two, if the surfactants are chemically adsorbed to the surface of the mineral, it may be very difficult to remove them. This is somewhat supported by the observation that the total organic carbon content for solids I, solids II and solids III were the same (1). The adsorbed surfactant would then determine the charge characteristics of the particles, leading to similar mobility.

Sedimentation Velocity, Sedimentation Rate and the Zeta Potential

For dispersions with a low volume fraction of solids the sedimentation velocity, sedimentation rate and the zeta potential are all closely related (7,8). For the case of high zeta potential, the particles sediment slowly and form a small volume of sediment. For the situation of low zeta potential, the dispersion is not stable, aggregates form and sediment quickly due to their mass but the final sedimentation volume will be large because of their inefficient packing.

Rather than using the zeta potential as a measure of colloidal stability, it may be better to measure the stability directly using a photometric dispersion analyzer. This instrument is especially valuable when dealing with surfaces whose charge originates from different sources, such as clays (9).

The zeta potentials of the solids from the sludge are all uniform despite the different settling rates. This suggests that the treatment with the different organic solvents may have altered the structure of the surfactants on the interface, enhancing sedimentation velocity. Alternatively, the treatment may have altered the surfactant structure on the surface such that polymer bridging may be enhanced, resulting in a larger degree of aggregation (10) hence faster sedimentation rates.

CONCLUSIONS

There is some surface active agent in the pond water that can change the electrokinetic properties of the solid/water interface. Mobilities of the solids dispersed in this pond water were all uniform.

No correlation between the zeta potential and sedimentation rate was found for solids that had been treated with organic solvent. Some difference between the solids, however, was found by examining the potentiometric titration curves and the change in ESA signal with increasing NaCl concentration. With increasing the solvent treatment, the buffering capacity of the solid surface increased and the amount of NaCl required to destabilized the dispersion decreased.

REFERENCES

1. Cerda, C.M., Fuhr, B.J., Pongar, K.C., and Schutte, R., Batch Settling Experiments of Tailings Sludge From the Hot Water Extraction of Oil Sands, Progress Report on CANMET Tailings sludge Project,1986.
2. Babchin, A.J., Chow, R.S., and Sawatzky, R.P., Adv. Interface and Colloid Science **30**(1989)111.
3. Williams, D.J.A. and Williams, K.P., J. Colloid and Interface Sci. **65**(1978)79.
4. Speyer, P., unpublished data.
5. Srinivasan, N.S., Spitzer, J.J., and Hepler, L.G., J. Can. Pet. Tech. **21**(1982)25.
6. Schramm, L.L. and Smith, R.G., Colloids and Surfaces **14**(1985)67.
7. Hunter, R.J., "Zeta Potential in Colloid Science", Academic Press, 1981.
8. Overbeek, J. Th G. in "Colloid Science", H.R. Kruyt, ed., Elsevier, 1952.
9. Chow, R.S., 'The Stability of Kaolinite in Water Dispersions', presented at the 63rd ACS Colloid and Surface Science Symposium, Seattle, 1989.
10. Gregory, J., J. Colloid and Interface Sci. **55**(1976)35.

VOLUME IV

THE EXTRACTION, CHARACTERIZATION AND INTERACTION OF HUMIC SUBSTANCES AND CLAYS FROM OIL SAND SLUDGES

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1. INTRODUCTION

Humic substances are geopolymers that occur naturally in soils, sediments and geological formations (Stevenson, 1982). These materials interact very strongly with metal ions and mineral surfaces through exchange and/or complexation processes. This interaction of the humic substances with mineral surfaces and metals could lead to the formation of stable and strong mineral-organic assemblages (Stevenson, 1982).

Oil sand sludges from the Fort McMurray ponds have been shown to contain significant amounts of minerals (sands, silts and clays), hydrocarbons and humic materials. The nature and properties of these components has been and still is the subject of active research in Alberta and elsewhere.

2. OBJECTIVE

The objectives of this project were to extract and characterize the humic substances and clays present in the solid phases of oil sand sludges, and to study the adsorption of sludge and commercially available humic materials on sludge and model clays.

To meet the above objective, humic substances and clays were isolated from a freeze dried sludge which has been extracted with toluene. The sludge humic materials were purified and later analyzed for elemental contents and functional groups and characterized by solid state 13-C NMR and FTIR spectroscopy. The clays were separated from the sludges and together with commercially available Kaolinite were cleaned and prepared for the adsorption experiments. Adsorption of sludge and Aldrich (commercial preparation) humic materials on kaolinte and sludge clays was also studied. The results of these activities are presented later in this report.

3. MATERIALS AND METHODS

3.1 MATERIALS

Sludge samples were obtained from the Oil Sands and Hydrocarbon Recovery Department of the Alberta Research Council. The samples originated from the tailing pond of Syncrude's Oil Sands Extraction Plant in Fort McMurray, Alberta. Wet sludge samples were extracted with toluene and freeze dried prior to the extraction of humic substances (Fuhr, 1989).

Commercially available humic substances were obtained from Aldrich Chemical Co and were subjected to the same cleanup steps as sludge humic materials. Kaolinite samples were obtained from the Oil Sands and Hydrocarbon Recovery Department of the Alberta Research Council and were treated similarly to sludge clays. These clays (Hydrite Kaolinites, Hydrite PX type of mean size 0.68 um) were obtained from Georgia Koalin, St Elizabeth, NJ.

3.2 EXTRACTION OF THE HUMIC SUBSTANCES

The extraction, isolation and purification of the fulvic and humic acids were according to procedures established by Schnitzer (1982), and were as follows.

3.2.1 Isolation

Two batches of samples (8 samples per batch) were used for the isolation of the humic substances. The procedures used for the two batches were similar except for a slightly higher number of isolation steps used for the second extraction.

A generalized flowchart for the extraction procedure of the humic substances is presented in Figure 1. The procedure consisted of mixing the sludge sample (50g) with 170 mL of 0.1 N NaOH in a 250 mL polypropylene centrifuge bottle, purging the suspension for 20 minutes with nitrogen gas, and shaking the capped bottles overnight (17-24 hours) in a table top shaker. The sludge mixture was centrifuged and the sludge supernatant and pellets were separated for further treatments. Further extractions of the pellets were done using either 0.1 N NaOH or distilled water and the resulting pellets recycled for extraction and the supernatant collected for humic/fulvic separation. The sludge pellets were characterized by a darker zone (rich organic layer) atop a greyish (mineral rich) layer. The dark zones of the pellets were collected and samples were further treated with 180 mL each of an HF/HCl solution (30 mL of concentrated acid/L). The pellets were finally discarded and the supernatants combined in order to separate the humic and fulvic materials.

Humic materials are defined as those that are soluble in alkali but insoluble in acid solutions, while fulvic materials are soluble under both alkali and acid conditions. Supernatants from the above extractions were acidified to pH 2.0 with 2N HCl which resulted in the precipitation of the humic materials. The suspension was left overnight to complete the precipitation of the humic materials, and later centrifuged at 12000 rpm for 15 minutes to separate the precipitated humic from the soluble fulvic materials.

3.2.2 Purification

Humic substances obtained from the previous step were purified by washing with a solution of HF/HCl (5mL of each acid per liter) and rinsing with distilled water. The humic materials were shaken overnight with the acid solution, centrifuged, and the resulting pellets rinsed and later freeze dried. The procedure was repeated several times in order to reduce the ash content of the humic material and convert it to an H^+ form.

The fulvic materials were concentrated from solution by passing (at pH 2.0) through a chromatography column packed with the macroporous resin XAD-8 (Servachrom-XAD from Serva Feinbiochemica, Heidelberg). The XAD-8 column retained the fulvic substances which were then eluted with 0.1 N NaOH. The concentrated fulvic materials were converted to the acidic H^+ form by liquid chromatography through

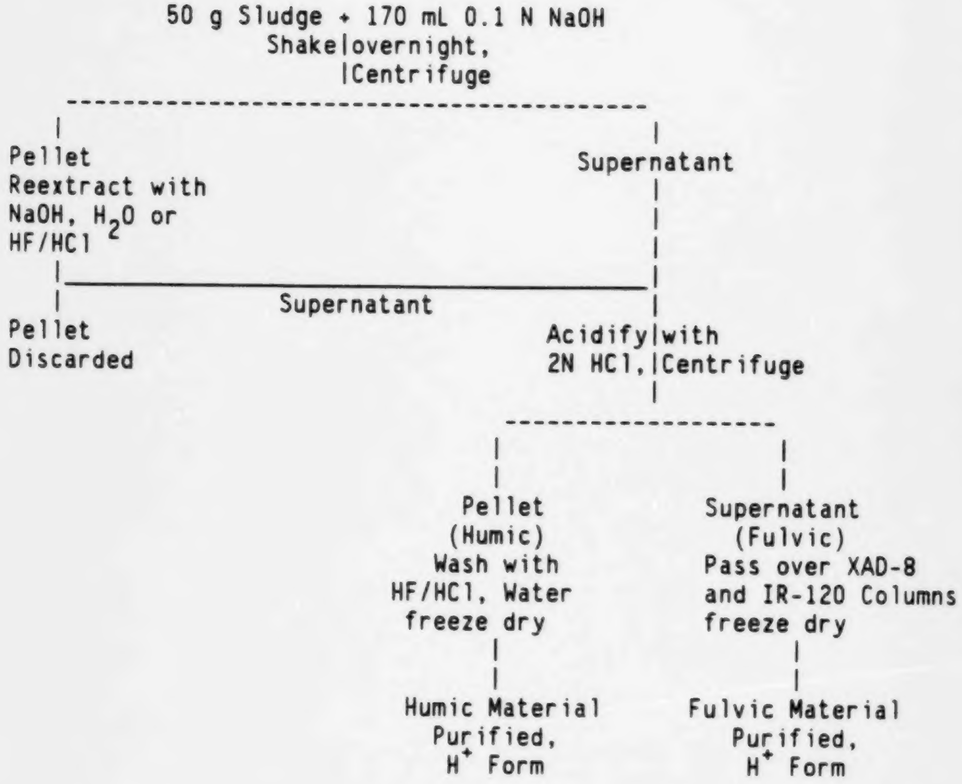


Figure 1. The flowchart of the procedures used for the extraction and purification of the humic substances.

a column packed with the anion exchange resin IR-120, and then freeze-dried.

Humic materials constituted the major portion of the recovered materials, while fulvic materials were showed very little recovery (40 mg.).

3.3 CHARACTERIZATION OF THE HUMIC SUBSTANCES

3.3.1 Elemental Analysis

Carbon, nitrogen, and hydrogen contents of the purified humic materials (H^+ form) were measured at the University of Alberta Chemistry Department using a Perkin-Elmer 240B analyzer and oxygen content with a Perkin-Elmer 240 analyzer converted for oxygen analysis.

Total carbon contents of several sludge separates and partially purified humic materials were measured with a LECO CR12 carbon analyzer.

Ash contents of the humic substances were determined after ashing for 4 hours in a muffle furnace at 700°C.

Total metal contents (including sulphur) were measured for a humic sample dissolved in a 0.04 M KOH solution using an Applied Research model 34000 Inductively Coupled Plasma Spectrometer.

3.3.2 Functional Groups

The total and carboxylic acidity of the humic materials were measured using barium acetate and calcium acetate titration, as reported by Schnitzer (1982). The difference between total and carboxylic acidity was attributed to phenolic hydroxyl groups (Schnitzer, 1982). The steps used in this procedure differed from Schnitzer's in that the addition of 10 to 30 mL aliquots was done with a 30 mL graduated Manostat syringe, and the filtering was done with a

Millipore Swinnex w/o filter cartridge equipped with a 0.45 um Millipore HA type filter membrane. These two additions to the basic procedure were necessary due to the nature of our samples (small differences in titration volumes encountered).

The total acidity determinations were done as follows:

i) Total acidity: A 0.15 M solution of $Ba(OH)_2.8H_2O$ in CO_2-free deionized water was prepared, heated to aid dissolution, and allowed to cool under a CO_2 trap (soda lime). After displacement of the air with N_2 in a 250 mL polypropylene bottle, the solution was centrifuged at 3000 rpm for 15 minutes to remove any solid $BaCO_3$ formed. Aliquots of 25 mL were then transferred by Manostat syringe to a blank and to a 50 to 80 mg purified HA sample in a 50 mL round bottomed distillation flask, purged with N_2, sealed, and then magnetically stirred for 24 hours. After filtration and rinsing with warm CO_2-free deionized water, the remaining $Ba(OH)_2$ was titrated (under N_2) with 0.5 N standardized (Na_2CO_3 method) HCl to a pH of 7.4. This was carried out in a three neck distillation flask with one neck sealed, one for the buret, and the other for the pH electrode.

The total acidity (mequivalents/g sample) was calculated from the difference between the blank and the sample titration volumes (mL).

$$\text{Total Acidity} = \frac{(\text{Vol. Blank} - \text{Vol. Sample}).(\text{N of acid}).1000}{\text{Sample weight (mg)}}$$

ii) Carboxylic acidity: 10 mL of a 1 M calcium acetate solution and 40 mL of CO2 free deionized water were added to both a blank and a 50 to 75 mg sample in a 50 mL round bottomed distillation flask were added , purged with N_2, sealed, and magnetically stirred for 24 hours. After filtration and rinsing, the solutions were titrated with 0.1 N standardized (KHP method)

NaOH to a pH of 9.8. The carboxyl acidity was calculated from the difference between the sample and the blank volumes used in the titration step.

$$\text{Carboxyl Acidity} = \frac{(\text{Vol. Sample} - \text{Vol. Blank}).(\text{N of acid}).1000}{\text{Sample weight (mg)}}$$

3.3.3 Spectroscopy

The 13-C solid-state NMR spectra were obtained on approximately 200 mg of freeze dried HA with 200 MHz Bruker Pulse CPX NMR spectrometer using magic-angle spinning and cross polarization. A contact time of 1 msec, sweep rate of 4000 Hz, and a spinning speed of 4.5 MHz and 2 bars pressure (Sapphire rotor) were used, with from 5000 to 15000 free induction decay curves collected.

FTIR spectra of FA and HA were obtained for KBr pressed pellets (2 mg HA or FA per 400 mg KBr) using a Bio-Rad FTS Fourier Transform Infrared Spectrometer.

3.4 CLAY SEPARATION

Size separation of clays requires that samples are free of interfering materials that might bind clays or impede their flocculation. Thus interfering materials such as carbonates, soluble salts, oxides and organic materials were removed from the clay samples prior to separation. Kaolinite clays which were obtained as a virtually "clean" clays, were also subjected to the same cleaning process as sludge clays to insure uniformity of treatments.

3.4.1 Removal of Carbonates and Soluble Salts

Carbonates and soluble salts were removed from the samples using the methods of Gee and Bauder (1986).

Kaolinite or freeze-dried sludge (200 g) were suspended in DDI water (1500 mL), and about 150 mL of 1 M NaOAc (pH 5) were added and the mixture shaken for one hour at 65°C. After centrifugation of the mixture in polypropylene bottles at 3000 rpm for 30 minutes, salinity measurements on the supernatants were checked using a conductivity meter (CDM83 Conductivity Meter, Radiometer, Copenhagen). The pellets were washed again and resuspended in 150 mL of DDI water then centrifuged as before. Washings were repeated until the conductivity measurements were less than 5% of the initial values (50μS/cm for an initial reading of 11000 μS/cm with the Kaolinite supernatants).

3.4.2 Removal of Organic Matter

The removal of organic matter was done according to the procedure reported by Gee and Bauder (1986).

The combined pellets from the above procedure were stirred for 3 hours at 50°C in 200 mL of DDI water and 250 mL of 35% H_2O_2. This treatment continued until cessation of frothing (freeze-dried sludge needed 2-3 L). After centrifugation in polypropylene bottles at 3000 rpm for 20 minutes, the pellets were washed with 150 mL of DDI water and centrifuged again at 5000 rpm for 15 minutes.

3.4.3 Removal of Metal Oxides

Oxides were removed from the samples according to the method used by Gee and Bauder (1986).

The washed pellets from above were transferred to a beaker using about 150 mL (for each pellet) of a citrate-bicarbonate buffer (0.27 M sodium citrate, 0.11 M sodium bicarbonate). About 10g of sodium dithionite were then gradually added to the mixture and heated to 80°C with mixing for 30 minutes. Upon cooling, 100mL of a saturated NaCl solution were added to the mixture, stirred for 30 minutes, and then centrifuged at 5000 rpm for 15 minutes.

3.4.4 Size Separation of Clays

The procedure followed for the size segregation of the mixtures was accomplished according to the methods of Jackson (1969).

i. Separation by sieving, sedimentation and decantation

a) Separation of sands from silt and clay

After resuspension in 1 L of a dilute sodium acetate solution (0.11g/L, pH 9.5), the sand fractions were separated as those particles greater than 45 μm. This was done by wet sieving of the mixtures through a 325-mesh sieve of 45 um opening width (The W.S. Tyler Company of Canada Ltd., Canadian Standard Sieve Series, St. Catharines, Ontario). The Kaolinite was not sieved as there were very few particles greater than 5 μm in the sample.

b) Separation of coarse silts

The supernatants of (a) containing particles less than 50 μm were further separated by settling for 7 minutes, followed by a careful decantation. The sediment contained particles between 50 and 20 μm (coarse silts), and the decantate contained those less than 20 μm. This separation was not necessary for the Kaolinite.

ii) The supernatant of (b) was further separated by centrifugation with swinging bucket and angle-head rotors.

a) Separation of medium and fine silts

The supernatants of (i-b) above were centrifuged at 750 rpm for 3 minutes. The pellets contained particles between 20 and 2 µm (medium and fine silt) whereas the supernatant contained those less than 2 µm.

b) Separation of coarse clays

The supernatants of (a) above were centrifuged at 2400 rpm for 30 minutes. The pellets contained particles between 2 and 0.2 µm (coarse clays) and the supernatants those less than 0.2 µm.

c) Separation of medium and fine clays

The supernatants of (b) above were centrifuged in an angle-head rotor at 15000 rpm for 30 minutes. The pellets contained particles between 0.2 and 0.08 µm (medium clays), whereas the supernatants contained the fine clays (less than 0.08 µm).

All the clay fractions were washed in deionized water, centrifuged at the appropriate rpm, frozen, and then freeze-dried.

3.5 ADSORPTION EXPERIMENTS

Mixtures of clays and humic substances were allowed to reach equilibrium for 17 to 24 hours (determined previously) prior to the analysis of HA adsorption or desorption. A clay concentration of 0.5 g per 25 mL of sample (in centrifugation tubes) was found best suited for the studies of adsorption with the Kaolinite. This was done by adding 12.5 mL of a suspended clay mixture (16g clay in 400 mL of buffer, adjusted to pH 8) to the 50 mL polypropylene centrifuge tube. The buffer was made up to resemble conditions present in the original sludge (3mM NaCl, 16 mM $NaHCO_3$ and pH 8). HA stock solutions were made as 480 mg/L at pH 8 also. All stock solutions were prepared one day in advance and the pH readjusted if necessary prior to mixing. Appropriate volumes of HA stock and buffer were added to bring the final volumes to 25 mL, a listing of which is presented in Table 1.

Table 1. Volumes of the stock solutions of clay (0.04 g/mL), HA (480 mg/L) and buffer (3mM NaCl; 16 mM $NaHCO_3$) used to make up the 25 mL samples for adsorption studies.

[HA]	Volume Added (mL)		
(mg/L)	HA	Buffer	Clay
10	0.52	11.98	12.50
25	1.30	11.20	12.50
50	2.60	9.90	12.50
80	4.17	8.33	12.50
110	5.73	6.77	12.50
140	7.29	5.21	12.50
170	8.85	3.65	12.50
240	12.50	0.00	12.50

The clay and humic mixtures (25 mL) were shaken overnight (17-24 hours) on a table top shaker. After centrifugation at 15,000 rpm for 10 minutes, the absorbencies of the supernatants were measured at 460 nm on a Spectronic 20 for determining the HA content present. The difference between the residual HA in solution after centrifugation and the HA added was taken as the amount of HA adsorbed to the clay samples. A standard curve for the HA solution was prepared using the same concentrations of HA listed in Table 1, except that the clay was replaced by a 12.50 aliquot of buffer. These standards were subjected to the same centrifugation period as the samples since there was formation of a very small pellet. Absorbencies before and after centrifugation are listed in Table 2 for both the purified Aldrich HA and the Sludge HA. For determining HA concentrations after centrifugation, values obtained for HA standards after centrifugation were used.

Table 2. Absorbencies (460 nm) for the HA concentrations listed in Table 1 for the purified Aldrich HA and the Sludge extracted HA before and after centrifugation at 15000 rpm for 10 minutes.

	ABSORBENCIES (460 nm)			
[HA]	Purified Aldrich HA		Extracted Sludge HA	
(mg/L)	before	after	before	after
10	0.0713	0.0645	0.097	0.080
25	0.177	0.160	0.243	0.194
50	0.350	0.319	0.496	0.363
80	0.550	0.496	0.750	0.560
110	0.727	0.656	0.996	0.772
140	0.945	0.851	1.29	0.960
170	1.14	1.03	1.52	1.18
240	1.55	1.40	2.05	1.66
avg. diff.	9.5 %		22.5 %	

Four sets of clay-HA mixtures were investigated. Two clays, from the Kaolinite and the Sludge were allowed to absorb with two separate HA solutions, the purified Aldrich HA and the sludge-extracted purified HA. All four sets had identical aliquots of the three stock solutions added as listed in Table 1.

4. RESULTS AND DISCUSSIONS

4.1 HUMIC MATERIALS

The amounts of purified HA obtained from the two extractions of the sludges were 523 and 700 mg respectively, for a total of 1.223 g, and a total of 40 mg fulvic material from the first extraction. The total carbon content of the sludge and HA were 3.1 and 65 % respectively, indicating an extraction efficiency of only 3.3 %. The low extraction efficiency is due in part to losses during the extraction procedure, presence of non-humic organic compounds (hydrocarbons, carbohydrates); and is indicative of very strong bonding between the humic and mineral phases. Thus most of the organic material is tightly bound to the fine minerals of the dried sludge so as to be unavailable even after many extractions and an HCl/HF pretreatment. Therefore, this remaining organic material is in fact similar to kerogen, a very difficult organic substance to isolate (Durand and Nicaise, 1980).

Elemental composition of the humic material is reported in Table 3 and compared to the results reported by Majid and Ripmeester (1987) for humic materials extracted from oil phase solids (OPS). Both HA's in Table 3 show a higher carbon content and lower nitrogen and oxygen contents than reported for most soil extracted HA (Schnitzer and Khan, 1972), while showing similar composition as those extracted from coal-like substances (Majid and Ripmeester, 1987). The high Barium content of the HA (Table 3) might cause errors (underestimation) in the determination of total and carboxyl acidity since the Ba seems to be bound to these groups, masking them during titrations. The sulfur content of the purified HA (2 %) was higher than those reported (perdue, 1985) for soils (< 1%). This increase is most likely due to losses of non-sulfur compounds in general and not to the introduction of sulfur from another source (Orr, 1978). The HA nitrogen content (4.48 %) is higher than reported for soil HA (<2 %).

Total and carboxyl acidity values of the humic material were 5.5 and 2.9 meq/g respectively. Half of the carbon, or 27.3 mmol/g is

Table 3. Elemental composition of humic acids from freeze-dried sludge, and other results reported in Majid and Ripmeester (1987) for humic acids extracted from oil phase solids (OPS).

Element	HA	HA (OPS)
	%	
C	65.43	67.37
H	4.48	4.40
N	2.29	1.00
O	21.35	24.23
S	1.94	3.00
Ba	0.34	NA*
Ti	0.40	NA
Sn	0.15	NA
Fe	0.05	NA
Al	0.05	NA
Ash	1.34	< 2.0
Total	97.82	NA

NA = Not available

equivalent to about 4.6 mmol/g benzene rings. Given the preponderance in nature for mono and non-hydroxyl aromatic substances, it is unlikely that the phenolic-OH content is more than this 4.6 mmol/g, and can be estimated by difference between total acidity and carboxyl contents to be about 2.6 mmol/g. Total unsaturation for our sample was 34 mmol/g, 10mmol/g of which can be accounted for as the aromatic carbon in the sample (4 mmol/g of unsaturation per 6 mmol/g of aromatic carbon) (Perdue, 1985). This leaves 24 mmol/g of unsaturation in other groups. At least 24 - 5.5, or 18.5 mmol/g, of unsaturation is present but not titrated as total acidity. These are possibly due to -C O groups, esters, amides (high nitrogen content), cycloalkyl groups, pyranose and furanose rings, amongst others (Perdue, 1985).

An early FTIR scan of the dried HA from extraction II is presented in Figure 2, where the HA was not sufficiently purified as indicated by the band just above 1000 cm^{-1}, possibly due to Si-C stretching (probably due to the presence of clay adsorbents). Three further HCl/HF washings proved necessary in order to remove this contamination as is shown in Figure 3, and evidenced by the low ash content of this sample (Table 3). The spectra for the purified FA is presented in Figure 4, and assignments of the various bands for both the HA and the FA of Figures 3 and 4 are presented in Tables 4 and 5 respectively following the guidelines established by MacCarthy and Rice (1985).

These spectra are almost identical to those obtained for a humic acid by Kotlyar et al (1988) which were obtained directly from an oil sands feed. These are reproduced for comparison purposes in Figure 5. Splitting at 1600-1700 cm^{-1} (in both Figures 3 and 5) suggests metal-HA bonding, a feature not observed with the purified FA in Figure 4. This could be due to some insoluble silicon, iron or aluminum too tightly bound to be removed under ordinary procedures, but yet not hindering the HA's overall solubility characteristics.

C-13 CPMAS/NMR results for the purified HA are presented in Figure 6 with assignments for the various peaks presented in Table 6.

It can be seen that almost 50 % of the substance is aromatic when comparing the aromatic carbon peak at 129 ppm with that for the aliphatic carbon at 31 ppm. There are also peaks for carbonyl at 154 ppm, carboxylic at 172 ppm and what appears to be carbohydrate at 72 ppm. Dipolar dephasing of protons was performed on the same sample and the results are presented in Figure 7. It can be seen that most if not all of the aliphatic carbon is protonated and that most if not all of the aromatic carbon is substituted.

A rigorous assumption for the amount of unsaturated carbon in an organic mixture was shown by Perdue (1984) to be given by;

$$a(total) = C(total) + N(total)/2 - H(total)/2 + 1000/Mn$$

where C, N, and H are the carbon, nitrogen, and hydrogen contents in mmol/g respectively, and Mn is the number-average molecular weight of the humic material. The amount of unsaturated carbon in mmol/g is designated as "a". For our sample, this calculates to be 34 mmol/g (data in Table 3), and assuming an Mn of 1000 g/mole. The aromatic constant of our sample can be estimated, from C13-NMR results, to approximate 50 % (Figure 6).

Table 4. Spectral assignments for FTIR spectra of purified HA.

Wavenumber	Assignments
3414	-OH stretching, broadness due to hydrogen bonding -phenolic and alcoholic OH groups
2923-2855	-stretching of C-H bonds in methyl/methylene units
1702-1617	-carbonyl oxygen, mainly COOH -1617 probably due to Si- or Fe- bonds to the COOH
1438-1376	-bending vibration of aliphatic C-H
1222	-C-O stretching and OH bending of carboxyl groups
1034	-Si-OH
765	-R3-Si-H

Table 5. Spectral assignments for FTIR spectra for the FA.

Wavenumber	Assignments
3405	-OH stretching -broadness due to hydrogen bonding -phenolic and alcoholic OH groups
2963-2938	-on OH 3405 shoulder, stretching of C-H bonds in methyl/methylene units
1716	-carbonyl oxygen stretching particularly of COOH units
1407	-bending vibration of aliphatic C-H groups
1206	-C-O stretching and OH bending due mainly to carboxyl groups
1042	-Si-OH stretching

Table 6. Assignments for carbon groups for the C13-NMR CPMAS spectra the purified HA in Figure 5.

Shift (ppm)	Assignment	
31	$-(CH_2)-$	aliphatic
72	-C-O-	carbohydrate
129	>C=	aromatic
154	C = O	carbonyl
172	CO -	carboxylic

Figure 2 FTIR spectra for the early purified HA with evidence of some contaminant near 1000cm^{-1}.

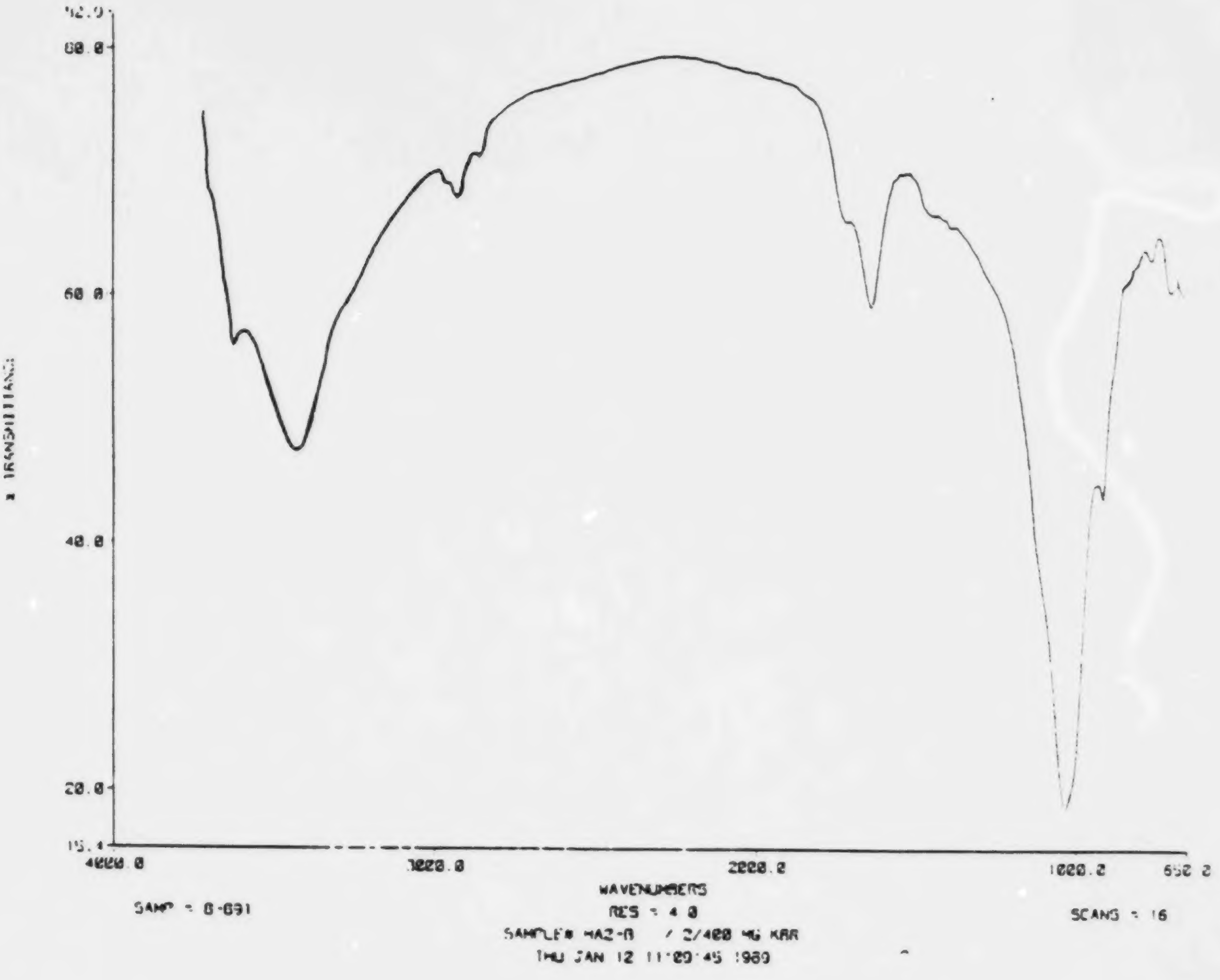


Figure 3 FTIR spectra for the purified HA.

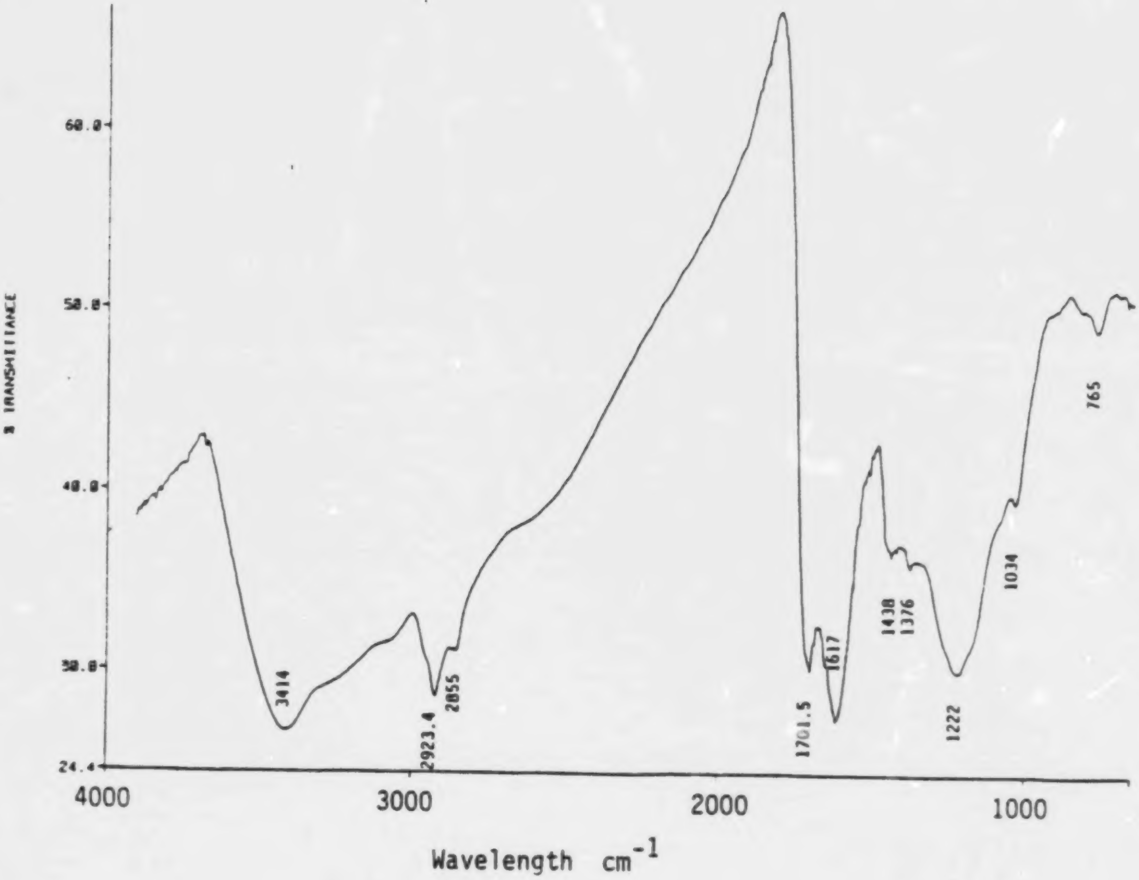


Figure 4 FTIR spectra for the purified FA.

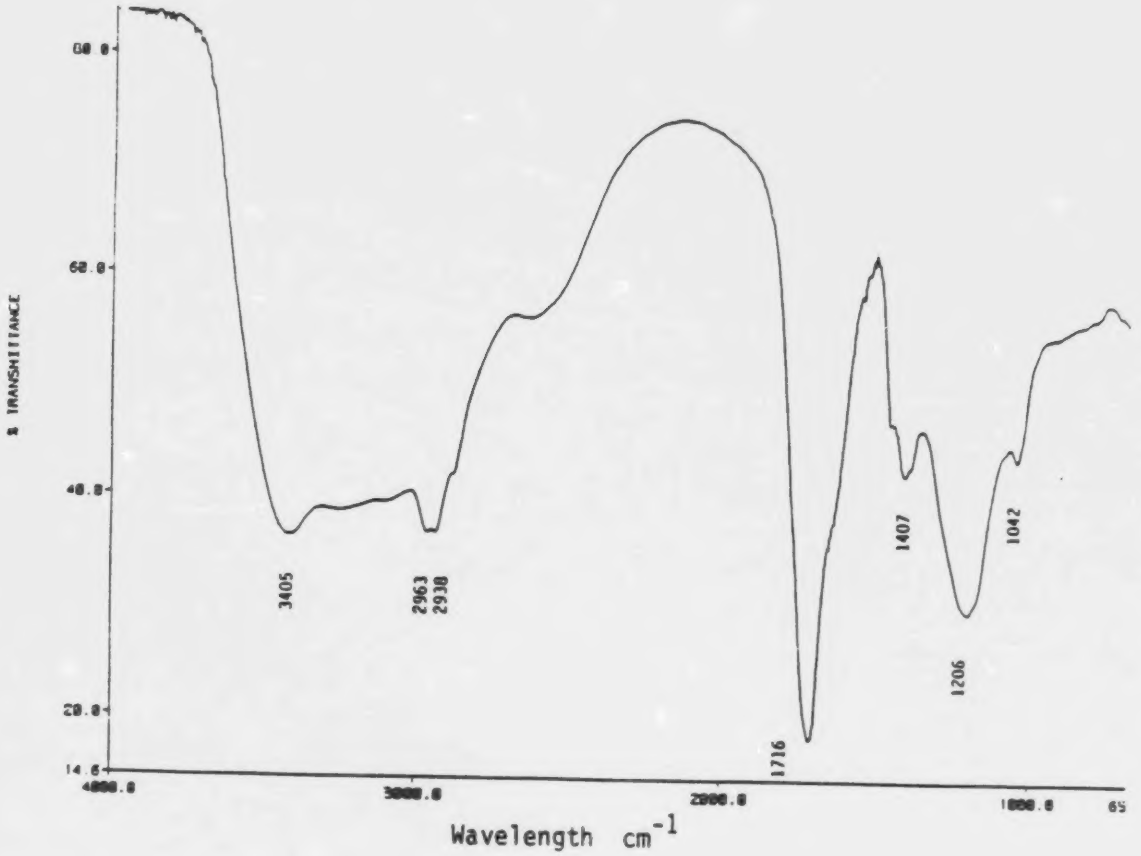


Figure 5 FTIR spectra for the purified HA from OPS as reported by Kotlyar et al. (1988).

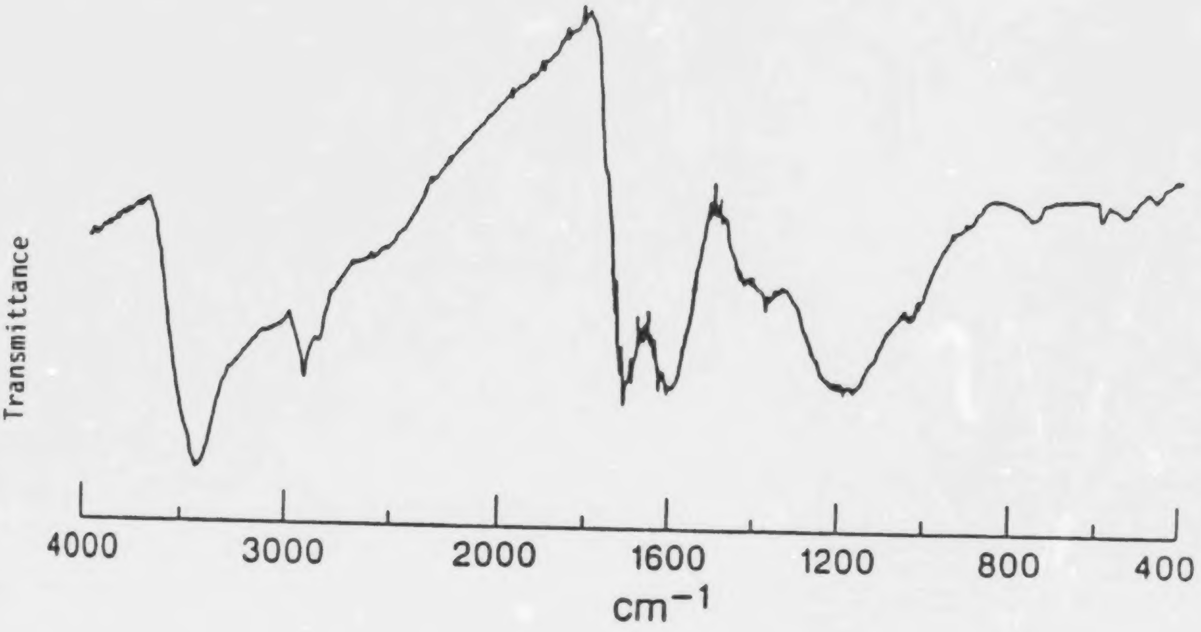


Figure 6 C-13 CPMAS/NMR spectra for the purified HA of figure 3.

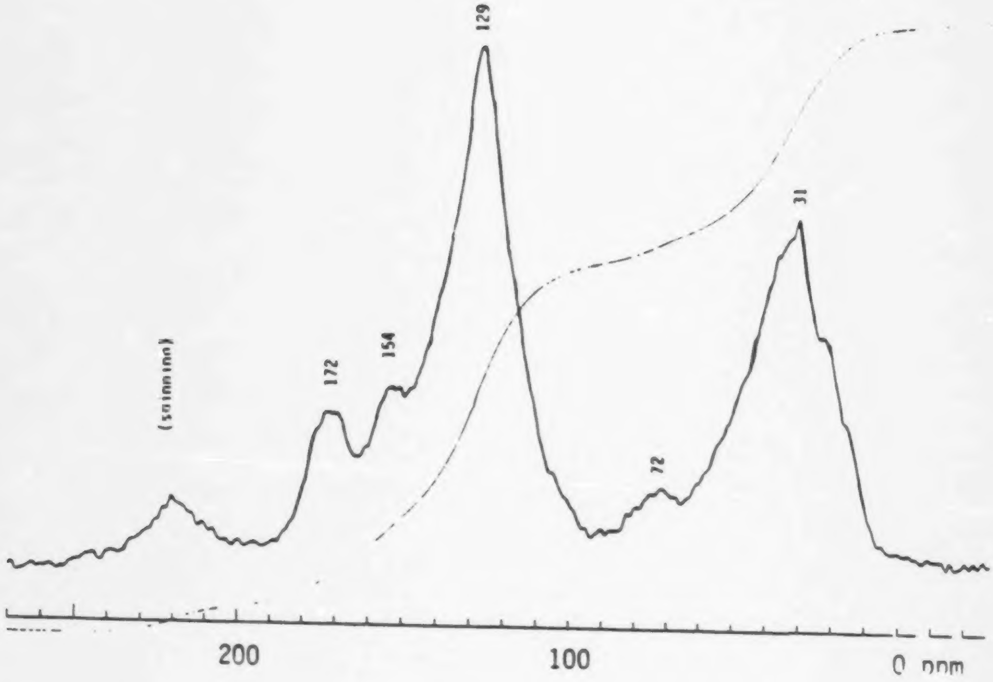
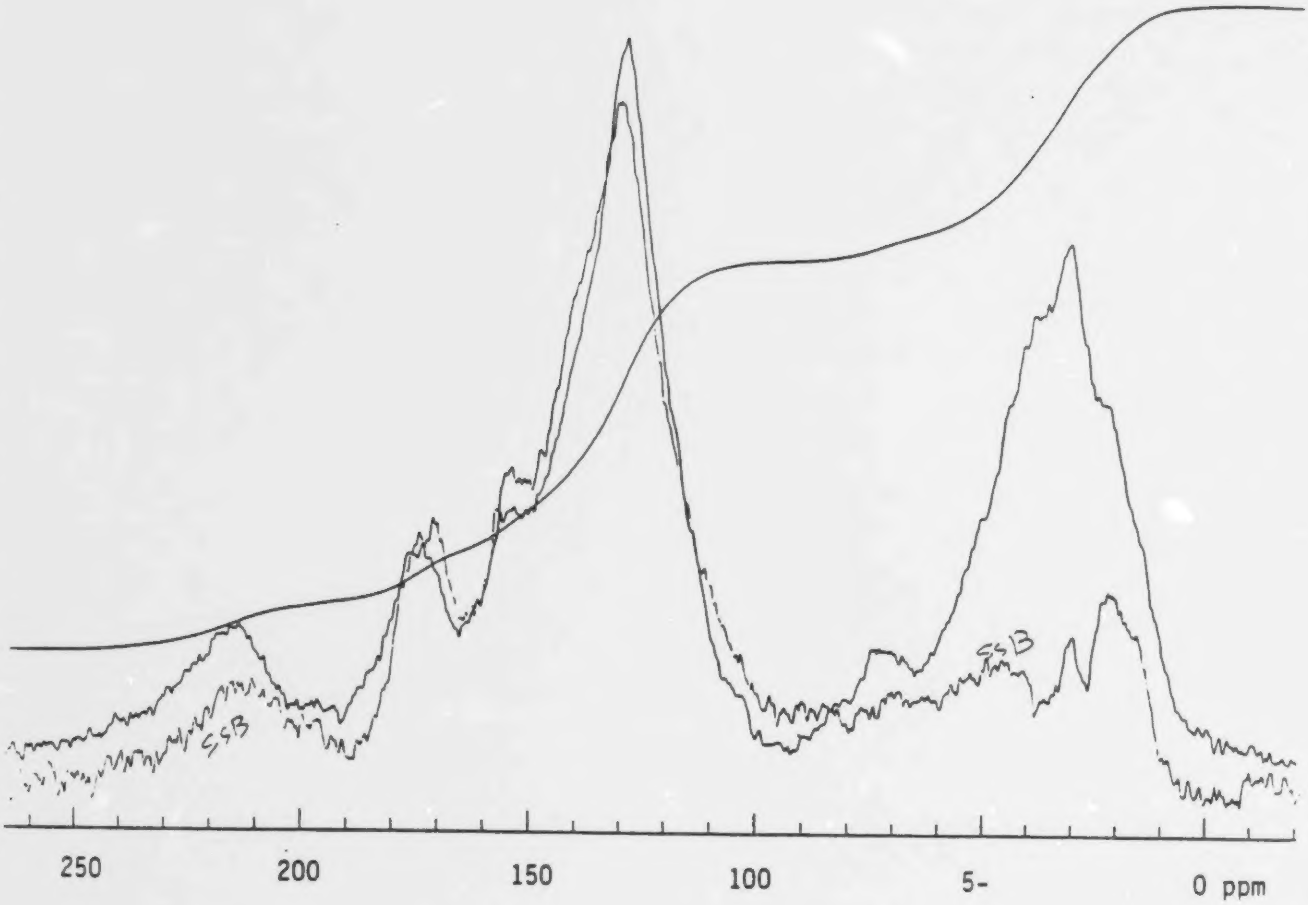


Figure 7 C-13 CPMAS/NMR proton dipolar-dephasing spectra of the HA also shown in figure 6.



4.2 ADSORPTION OF HUMIC MATERIALS TO CLAYS

The amounts of various size fractions obtained from the Kaolinite and the sludge are presented in Table 7. The Kaolinite, as expected, had most of its clays in the 0.2 to 2 µm range (coarse clays); whereas the sludge exhibited a wider distribution between 0.08 and greater than 20 µm. The original amounts of Kaolinites and sludges used were 190 and 200 g respectively (Table 7), but the need for more clays necessitated a further extraction of another 400 g of kaolinites and sludges. The other Kaolinite and sludge samples showed identical particle size distributions to those of the original extraction (Table 7). All size fractions for the Kaolinite were white colored, whereas some grayness was evident for all the sludge size fractions. The fine clay pellets had an exceptionally dark gray surface as compared to other fractions of the sludge. These fractions were resuspended in H_2O_2 for 24 hours then centrifuged (15,000 rpm for 15 minutes). Once the dark gelatinous surfaces (organic layers) of these pellets were removed, the remaining white colored pellets were combined and further resuspended in H_2O_2 for 24 hours. After centrifugation, the pellets were resuspended in the Na_2CO_3 solution, recentrifuged, then freeze-dried.

Carbon percentages were determined for the various size fractions to ascertain the purity of the clays and are reported in Table 8. The additional treatment of the sludge dark gray fine clay pellets (0.20 to 0.08 µm) with H_2O_2 was evidently beneficial, as it reduced the carbon content significantly (0.34 to 0.04%). The highest amount of carbon (0.47 %) was observed with the fine silt fraction (2 to 5 µm) whereas the least (0.14 %) was with the coarse clay fraction (0.2 to 2 µm). The high carbon content (0.34%) of the sludge fine clay fraction shows the strong binding of the humic materials to these clays.

Table 7. Weight of starting material, sand, silt, and clays obtained by size fractionation of Kaolinite and freeze-dried sludge.

Size classification	Kaolinite (190 g)		Sludge (200 g)	
Coarse silt to heavy sand (> 20 μm)	0.0	(0 %)	44 g	(22 %)
Medium silt (5 to 20 μm)	0.0	(0 %)	21 g	(10 %)
Fine silt (2 to 5 μm)	18 g	(9 %)	25 g	(13 %)
Coarse clay (0.2 to 2 μm)	163 g	(86 %)	40 g	(20 %)
Fine clays (0.08 to 0.2 μm)	1 g	(0.5 %)	5.2g	(10 %)
Lost, organics, and/or oxides	8 g	(4.2 %)	50 g	(25 %)

Table 8. Carbon contents for the various size fractions isolated from the sludge and the Kaolinite.

Size Fraction	Total Carbon (%)
Original sludge	3.14
greater than 5 µm	0.34
2 µm to 5 µm	0.47
0.2 to 2 µm	0.15
0.2 to 0.08 µm	
before extra H_2O_2	0.34
after extra H_2O_2	0.14
after extensive H_2O_2	0.04
KAOLINITE, 0.2 to 2 µm	0.07

Results for the adsorption of the purified Aldrich HA to the Kaolinite clay fraction are presented in Table 9. The absorbencies (at 460 nm) of the remaining HA solutions were transformed into HA concentration values (mg/L) using an HA standard curve of absorbencies of known HA concentrations. The adsorbed HA concentration (mg HA/g Clay) were calculated from the added and remaining HA solution concentration by difference. Note that the values reported for the Kaolinite-Sludge binding results are initially slightly less than the corresponding results obtained with the Kaolinite-Aldrich HA case (Table 9), but that the maximum binding values for the Kaolinite-Sludge HA eventually exceed those of the Aldrich HA at 110 mg/L of initial HA concentration. This is probably due to the fact that the Sludge HA loses more (22.5%) than does the Aldrich HA (9.5%) upon centrifugation (Table 2). The result of this is that at lower concentrations (< 110 ppm HA), there is in fact less HA of the "soluble" type available to approach maximum binding capacity than there is with the more "soluble" Aldrich HA. This difference is not due to changes in functional groups as the FTIR spectra of the two HA's were almost identical (there were no acid titrations performed on the Aldrich HA). A more plausible explanation of these differences could be the nature of the metallic ions complexed with the HA's and the resulting changes in molecular aggregation and thus size.

The maximum binding capacity for both Aldrich and sludge HA with Kaolinite clays was almost the same, 1.19 and 1.18 mg/g respectively. The Kaolinite-Aldrich maximum binding result was calculated using only the last two entries in Table 9, whereas that for the Kaolinite-Sludge is only the last entry.

Table 10 shows the results for the adsorption of Aldrich and Sludge HA to Sludge clays. The high absorbencies and interferences (precipitation upon centrifugation) render this data less easily interpretable. The data indicates less maximum binding than for Kaolinites. Differences between Aldrich and sludge HA adsorption are not easily discernible as the remaining solution concentrations calculated were close to those added.

Table 9. Amounts of purified Aldrich HA or purified sludge extracted HA adsorbed to the 0.5 g of Kaolinite clay after 24 hours of equilibration.

	-- Kaolinite - Aldrich HA --			--- Kaolinite - Sludge HA ---		
initial [HA] (mg/L)	Abs. 460 nm n=3	Solution [HA] (mg/l)	mg HA per g-clay	Abs 460 nm n=3	Solution [HA] (mg/l)	mg HA per g clay
10	0.0164	2.54	0.373	0.0483	4.55	0.272
25	0.0700	10.9	0.708	0.121	11.4	0.679
50	0.211	33.0	0.850	0.330	33.8	0.810
80	0.381	59.7	1.02	0.569	62.4	0.877
110	0.555	89.5	1.03	0.755	86.2	1.18
140	0.717	120	1.00	1.10	NR	NR*
170	0.876	144	1.29	1.34	NR	NR
240	1.27	218	1.08	1.89	NR	NR
AVERAGE MAXIMUM mg HA per g			1.19			1.18

* NR = Not reported due to very high absorbance values and uncertainties.

Table 10. Amount of purified Aldrich HA or sludge extracted HA adsorbed to 0.5 g of sludge coarse clays (0.2 to 2μm) after 24 hours of equilibration.

	--- Kaolinite - Sludge HA ---			--- Sludge Clay - Sludge HA --		
initial [HA] (mg/l)	Abs. 460 nm (n)	Solution [HA] (mg/L)	mg HA per g-clay	Abs 460 nm (n)	Solution [HA] (mg/L)	mg HA per g-clay
10	0.062 (3)	9.7	0.015	NR	NR	NR
25	0.157 (2)	24.6	0.020	0.175 (1)	22.5	0.121
50	0.316 (1)	49.5	0.023	0.346 (2)	47.7	0.115
80	0.491 (2)	79.3	0.036	0.556 (2)	79.5	0.030
110	0.670 (3)	110.0	0.000	0.772 (2)	110.0	0.000
140	0.843 (1)	138.6	0.069	0.987 (1)	140.0	0.000
170	1.0 (2)	165.9	0.205	NR	NR	NR
240	1.4 (2)	240.0	0.000	NR	NR	NR

NR = Non-recoverable data.

Attempts at desorbing the adsorbed HA by resuspending the adsorbed HA-clay complex in solution (minus the clay and HA) were not successful as the HA is very strongly bound to the clay surfaces. Release of the adsorbed HA to the desorbing solution was negligible (no absorbance measured at 460 nm). This was true for the HA adsorption on both Kaolinite and sludge clays.

The technique used for calculating the maximum binding of HA to Kaolinite clays is crude at best, for the absorbance values of the HA solutions are not accurate enough to discern expected differences. A more useful approach would necessitate a measurement of the organic carbon present in solution (sensitivity of few μg to mg per L) and the calculation of adsorbed HA from solution differences. We attempted to do this with stored samples, but encountered interferences from the solution carbonates ($NaHCO_3$). Attempts to take the carbonates out of solution by acidification led to further problems of HA precipitation. As it stands, one should consider these results as preliminary and more of a qualitative exhibit of the conditions studied.

5. REFERENCES

Durand, B. and G. Nicaise. 1980. Procedures for Kerogen Isolation, chapter 2 in "Kerogen. Insoluble Organic Matter from Sedimentary Rocks.", Durand, B., ed., Editions Technip, Paris., pp.35-53.

Fuhr, B. 1988. Personal communication. Alberta Research Council, Edmonton, AB.

Gee, G.W., and J.W. Bauder. 1986. Particle size analysis. Chapter 15 in "Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods", second edition. Agronomy Monograph Number 9, American Society of Agronomy and Soil Science Society of America, pp. 383-411.

Jackson, M.L. 1969. Mineral fractionation for soils. Chapter 3 in "Soil Chemical Analysis-Advanced Course", second edition, Published by the author, Madison, Wiss., 53705, 1979, pp. 100-165.

Johnson, D.W., and D.E. Todd. 1983. Some Relationships among Fe, Al, C and SO4 in a variety of forest soils. Soil Science Society of America Journal 47:702-800.

Kotlyar, L.S., J.A. Ripmeester, B.D. Sparks, and D.S. Montgomery. 1988. Characterization of Oil Sands Closely Associated with Athabasca Bitument. Fuel 67:808-814.

MacCarthy, P. and J.A. Rice. 1985. Spectroscopic Methods (other than NMR) for Determining Functionality in Humic Substances. chapter 21 in "Humic Substances in Soil, Sediment and Water.", Eds.; Aiken, McKnight, Wershaw; MacCarthy, John Wiley and Sons, NY, pp. 539-543.

Majid, A. and J.A. Ripmeester. 1987. Characterization of Humic Matter Associated with Heavy Metals from Oil Sand. ACS Symposium Series, vol. 344, Met. Complexes, Fossil Fuels, pp. 290-306.

Orr, W.L. 1978. Sulfur in Heavy Oils, Oil Shale, and Oil Sands, in " Oil Sand and Oil Shale Chemistry", Verlag Chemie, N.Y, p. 238.

Perdue, E.M. 1984. Analytical Constraints on the Structural Features of Humic Substances. Geochim. Cosmochim. Acta 48:1435-1442.

Perdue, E.M. 1985. Acidic Functional Groups of Humic Substances, chapter 20 in "Humic Substances in Soil, Sediment and Water", eds., Aiken; McKnight, Wershaw; MacCarthy. John Willey and Sons, NY, 692 p., pp. 539-543.

Schnitzer, M. 1982. Organic Matter Characterization. Chapter 30 in "Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties", second edition, edited by A.L. Page. Agronomy Monograph Number 9, American Society of Agronomy and Soil Science Society of America, pp. 581-593.

Schnitzer, M. and S.U. Khan. 1972. Humic Substances in the Environment. Marcel Dekker, NY.

Stevenson, F.J. 1982. Humus chemistry. John Wiley and Sons, New York.

VOLUME V

APPENDIX 1

List of all Settling Experiments from April 1988 Progress Report

The data for all these experiments, coded as in the EXPLOG data table, are on disk at the Alberta Research Council, Clover Bar.

The following descriptions/tables are explanations to the EXPLOG data table:

SV#: The settling vessel number.

SL from: source of the sludge:

1 - 86-12-01 sludge

2 - 86-12-02 sludge

4 - 86-12-04 sludge

5 - 86-12-05 sludge

BE - Batch extraction (Hot Pot) of 04-86-18 oil sand (SCL).

NomSL Conc.: Nominal sludge concentration - an approximate vol% of sludge in settling vessel (≃ 0.33 g solids / 1% SL concentration, hence values >100% when sample has been compacted) but actual values are used in calculations.

Dil.: Diluent used for either dilution of sludge or preparation of 'synthetic' sludge from dried solids.

DILUENT	DESCRIPTION
CWDO	Centrifuged sludge water deoiled by passing the water through a coffee filter with a #31 Whatman filter under it. Minimal oil and a few particulates are left in the filtrate.
CWF	Centrifuged sludge water filtered through a 0.45μ Millipore filter.
DH2O	Deionized water.
H2O2	Hydrogen Peroxide, 3 volume %.
HCL	A 10% by volume HCl solution was used to dilute and 'wash' the sludge solids.
MEOH	Methanol was added in a specific quantity to deionized water either as a diluent or as a 'wash' for sludge solids.
NAOH	Sodium Hydroxide was used either as a diluent or as a 'wash' for the sludge solids or as an additive in extraction of oil sand to generate sludge.

NONE	Sludge with no dilution or drying.

SOL. TYPE: Type of solids used in the experiment/settling vessel:

SOLIDS TYPE	DESCRIPTION
CSOD	Centrifuged sludge solids that are still oily and have been dried (evaporated).
CWDO	NOT a solid - centrifuged water deoiled.
DEC	Decant (24 hr) solids from deoiling by Wemco cell, <3.9μ.
I	Sludge solids that have been cleaned with a Toluene/IPA mixture.
II	Sludge solids that have been cleaned with a Toluene/IPA mixture followed by Methylene Chloride.
III	Sludge solids that have been cleaned with a Toluene/IPA mixture followed by Methylene Chloride then Methanol.
SED	Sediment (24 hr) solids from deoiling by Wemco cell, majority >3.9μ.
SL	Sludge passed through a 250μ sieve.
SLE	Sludge evaporated to dryness.
SLEA	Sludge evaporated to dryness then ashed @ 540°C.
SLFD	Sludge freeze-dried.
SLL	Sludge passed through a 90μ sieve.
WSL	Whole sludge.
ST	Secondary tailings.

Treat 1, 2, 3: The special treatment(s) used in the experiment (not necessarily in that order):

TREATMENT	DESCRIPTION
AL	Aluminum added in some form.
AMREM	Amorphous coatings removed.

AWASH	Acid wash.
COMP	Compacted solids by centrifuging.
DEK	Decanted the supernatant after 24 hr of settling.
DEKC	Decanted the supernatant from the coarse solids at a time >24 hr.
DEOIL	Deoiled using a Wemco cell.
DIL	Dilution.
DRAIN	Bottom drainage provided.
F#REM	Froth removed prior to subsampling.
FE	Iron added in some form.
FER	Iron removed at some point of the experiment.
FRTH	Freeze-thaw.
HEAT	Sludge heated to either 80°C or 100°C.
HCL	Hydrochloric acid added as some time of the experiment.
NONE	No treatment.
RECON	Reconstituted from dried solids.
REH2O	Replaced the water above the sludge (removed with a syringe) with deionized water. SV inverted and resettled (RESET).
SA	Spherical agglomeration technique using either SFC - Syncrude Fluid Coke - or ACC - Activated Cocoanut Charcoal.
STIR	Stirred prior to settling.
SWEL	Swelling of dried solids.
UF	Ultrafiltered.
VIBES	Vibrations applied.

SV Type: the size and material of the settling vessel.

1G	1 L glass graduate cylinder.
100G	100 mL glass graduate cylinder.
250G	250 mL glass graduate cylinder.
5GD	~5 L glass drainable cylinder.
1GD	1 L glass graduated drainable cylinder.
500GD	500 mL glass graduated drainable cylinder.
1MG	1 M tall glass cylinder (~vol = 0.5 L)
2MG	2 M tall glass cylinder (~vol = 4 L).
PS	100 mL Polystyrene graduate cylinder.
TLC	Thin layer chromatography development tank, rectangular (~vol = 800 mL).

LOG OF SETTLING VESSELS ACCORDING TO #.COMPOSITION AND TREATMENT

SV#	SL from	NomSL Conc.	DIL.	Sol Type	Treat 1	Treat 2	Treat 3	SV Type
A	1	100	NONE	WSL	NONE			2MG
1	1	80	CWF	WSL	DIL			1G
2	1	60	CWF	WSL	DIL			1G
3	1	40	CWF	WSL	DIL			100G
4	1	20	CWF	WSL	DIL			100G
5	1	5	CWF	WSL	DIL			100G
6	1	50	CWF	WSL	DIL			100G
7	1	40	CWF	WSL	DIL			100G
8	1	30	CWF	WSL	DIL			100G
9	1	20	CWF	WSL	DIL			100G
10	1	10	CWF	WSL	DIL			100G
11	1	5	CWF	WSL	DIL			100G
12	2	100	NONE	WSL	NONE			1G
13	2	100	NONE	WSL	VIBES			1G
14	1	40	CWDO	WSL	DIL			100G
15	1	20	CWDO	WSL	DIL			100G
16	1	40	DH20	WSL	DIL			100G
17	1	20	DH20	WSL	DIL			100G
18	1	40	CWF	WSL	AL			100G
18A	1	100	NONE	WSL	AL			100G
19	1	100	NONE	SL	NONE			PS
19A	1	100	NONE	SL	FRTH			PS
19B	1	100	NONE	SL	FRTH			PS
21	4	40	CWDO	SL	DIL			PS
22	4	20	CWDO	SL	DIL			PS
23	4	10	CWDO	SL	DIL			PSS
24	4	5	CWDO	SL	DIL			PS
25	4	40	CWDO	SL	AL	5000		100G
26	4	40	CWDO	SL	AL	3000		100G
[illegible]	4	40	CWDO	SL	AL	[illegible]		100G
28	4	40	CWDO	SL	AL	1000		100G
29	4	40	CWDO	SL	AL	500		100G
30	4	100	NONE	SL	FRTH	STIR		100G
35	4	40	DH20	SL	DEOIL	F1REM		PS
36	4	40	DH20	SL	DEOIL	F2REM		PS
37	4	40	DH20	SL	DEOIL	F3REM		PS
38	4	40	DH20	SL	DEOIL	DEK		250G
39	4	100	NONE	SL	DEOIL	F1REM		PS
40	4	100	NONE	SL	DEOIL	F2REM		PS
41	4	100	NONE	SL	DEOIL	F3REM		PS
42	4	40	DH20	SL	DEOIL	STIR		PS
43	1	100	DH20	I	RECON			PS
44	1	60	DH20	I	RECON	DIL		PS
45	1	40	DH20	I	RECON	DIL		PS
46	1	20	DH20	I	RECON	DIL		PS
47	1	5	DH20	I	RECON	DIL		PS
48	1	100	DH20	II	RECON			PS
49	1	60	DH20	II	RECON	DIL		PS
50	1	40	DH20	II	RECON	DIL		PS

EXPLOG (MR).2

LOG OF SETTLING VESSELS ACCORDING TO #,COMPOSITION AND TREATMENT

SV#	SL from	NomSL Conc.	DIL.	Sol Type	Treat 1	Treat 2	Treat 3	SV Type
51	1	20	DH20	II	RECON	DIL		PS
52	1	5	DH20	II	RECON	DIL		PS
53	1	100	DH20	III	RECON			PS
53A	1	100	DH20	III	FRTH			PS
53B	1	100	DH20	III	FRTH	REH20		PS
54	1	60	DH20	III	RECON	DIL		PS
55	1	40	DH20	III	RECON	DIL		PS
56	1	20	DH20	III	RECON	DIL		PS
56A	1	20	DH20	III	REH20	RESET		PS
57	1	5	DH20	III	RECON	DIL		PS
58	1	100	CWDO	I	RECON			PS
59	1	60	CWDO	I	RECON	DIL		PS
60	1	40	CWDO	I	RECON	DIL		PS
61	1	20	CWDO	I	RECON	DIL		PS
63	1	100	CWDO	II	RECON			PS
64	1	60	CWDO	II	RECON	DIL		PS
65	1	40	CWDO	II	RECON	DIL		PS
66	1	20	CWDO	II	RECON	DIL		PS
68	1	100	CWDO	III	RECON			PS
68A	1	100	CWDO	III	FRTH			PS
68B	1	100	CWDO	III	FRTH	REH20		PS
69	1	60	CWDO	III	RECON	DIL		PS
70	1	40	CWDO	III	RECON	DIL		PS
71	1	20	CWDO	III	RECON	DIL		PS
72	1	5	CWDO	III	RECON	DIL		PS
73	1	15	DH20	III	RECON	DIL		PS
73A	1	15	DH20	III	REH20	RESET		PS
74	1	10	DH20	III	RECON	DIL		PS
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	DEOIL	STIR		100G
76	4	40	DH20	SL	DEOIL	STIR		PS
77	4	40	DH20	SL	DEOIL	F1REM		100G
78	4	40	DH20	SL	DEOIL	F2REM		100G
79	4	40	DH20	SL	DEOIL	F3REM		100G
80	4	40	DH20	SL	DEOIL	DEK		250G
81	4	40	DH20	SL	DEOIL	DEK	HCL	250G
82	1	100	MEOH	II	RECON			PS
83	1	60	MEOH	II	RECON	DIL		PS
84	1	40	MEOH	II	RECON	DIL		PS
85	1	20	MEOH	II	RECON	DIL		PS
86	1	5	MEOH	II	RECON	DIL		PS
87	4	40	CWDO	SL	AL	250		100G
88	4	40	CWDO	SL	AL	150		100G
89	4	40	CWDO	SL	AL	100		100G
90	4	40	CWDO	SL	AL	50		100G
91	4	40	DH20	DEC	UF			100G
92	4	100	NONE	SL	FRTH			PS
93	4	100	NONE	SL	FRTH			PS
94	4	40	CWDO	SL	FRTH			PS

LOG OF SETTLING VESSELS ACCORDING TO #,COMPOSITION AND TREATMENT

SV#	SL from	NomSL Conc.	DIL.	Soi Type	Treat 1	Treat 2	Treat 3	SV Type
95	4	40	DH20	SL	FRTH			PS
96	4	40	DH20	DEC	FRTH	UF		PS
97	4	40	DH20	SED	DEK			100G
98	1	100	DH20	SLE	SWEL			100G
99	1	100	DH20	CSOD	SWEL			100G
100	1	100	DH20	I	SWEL			100G
101	1	100	DH20	III	FER	AMREM	RECON	100G
102	1	100	DH20	SLE	RECON			100G
103	1	100	DH20	CSOD	RECON			100G
104	4	20	CWDO	SL	FRTH			PS
105	4	40	CWDO	SL	FRTH			PS
106	4	60	CWDO	SL	FRTH			PS
107	4	80	CWDO	SL	FRTH			PS
108	4	100	NONE	SL	FRTH			PS
109	2	127	NONE	WSL	FRTH	COMP		PS
110	2	143	NONE	WSL	FRTH	COMP		PS
111	2	178	NONE	WSL	FRTH	COMP		PS
112	2	234	NONE	WSL	FRTH	COMP		PS
113	4	40	HCL	SL	FER	AWASH		100G
114	1	100	DH20	SLEA	RECON			100G
115	1	100	CWDO	SLEA	RECON			100G
116	4	60	DH20	SL	FER	SA	SFC5	100G
117	4	60	DH20	SL	FER	SA	SFC10	100G
118	4	60	DH20	SL	FER	SA	ACC5	100G
119	4	60	DH20	SL	FER	SA	ACC10	100G
120	1	100	DH20	III	RECON	HEAT		100G
121	4	60	DH20	SLL	FER	SA	SFC20	100G
122	4	60	DH20	SLL	FER	SA	SFC40	100G
123	4	60	DH20	SLL	FER	SA	ACC20	100G
124	4	60	DH20	SLL	FER	SA	ACC40	100G
125	4	60	DH20	SLL	DIL			100G
126	4	60	DH20	SLL	DIL	HCL		100G
127	4	100	NONE	SL	HEAT			100G
128	4	100	NONE	SL	HEAT	HCL		100G
129	4	40	NAOH	SL	DIL	1N		100G
129A	4	40	NAOH	SL	REH20	RESET		
130	4	40	NAOH	SL	DIL	.01N		100G
131	BE	5	DH20	ST	NONE			1G
132	BE	5	NAOH	ST	NONE	.01%		1G
133	BE	5	NAOH	ST	NONE	.02%		1G
133AL	BE	5	NAOH	ST	AL	DEKC		250G
133ALR	BE	5	NAOH	ST	AL	DEKC		250G
133FE	BE	5	NAOH	ST	FE	DEKC		250G
134	BE	5	NAOH	ST	NONE	.04%		1G
134AL	BE	5	NAOH	ST	AL	DEKC		250G
135	BE	80	DH20	ST	COMP			100G
135B	BE	80	DH20	ST	FRTH	COMP		PS
136	BE	80	NAOH	ST	COMP			100G
136B	BE	80	NAOH	ST	FRTH	COMP		PS

LOG OF SETTLING VESSELS ACCORDING TO #,COMPOSITION AND TREATMENT

SV#	SL from	NomSL Conc.	DIL.	Sol Type	Treat 1	Treat 2	Treat 3	SV Type
137	1	100	NAOH	II	RECON	REH20		100G
137B	1	100	NAOH	II	FRTH			PS
138	1	100	NAOH	III	RECON	REH20		100G
138B	1	100	NAOH	III	FRTH			PS
139	1	100	MEOH	II	RECON	REH20		100G
139B	1	100	MEOH	II	FRTH			PS
140	4	100	HCL	III	FER	AWASH	RECON	100G
141	4	0	CWDO		AL			100G
142	4	100	NONE	SL	NONE			1G
143	4	100	NONE	SL	NONE			TLC
144	4	100	NONE	SL	NONE			TLC
145	4	40	CWDO	SL	DRAIN			5GD
146	4	40	CWDO	SL	DRAIN			5GD
147	4	40	CWDO	SL	DRAIN			1GD
148	1	40	CWDO	SL	DRAIN			1GD
149	1	40	DH20	DEC	AL			250G
150	5	100	NONE	SL	AL			100G
151	1	40	CWDO	III	RECON	DIL		100G
152	1	40	CWDO	III	RECON	DIL	NAOH	100G
152A	1	40	CWDO	III	REH20	RESET		
153	5	40	NAOH	SL	DIL			100G
154	5	40	NAOH	SL	DIL	STIR		100G
155	5	40	H202	SL	DIL			100G
156	5	40	H202	SL	DIL	STIR		100G
157	5	0	NAOH	CWDO	DIL			100G
158	1	40	DH20	III	RECON	DIL	NAOH	100G
159	1	100	NAOH	SLE	RECON	REH20		100G
160	5	20	DH20	SL	DIL			1MG
[illegible]	5	40	DH20	SL	DRAIN			500GD
[illegible]	5	100	NAOH	SLFD	RECON	REH20		100G
175	5	40	CWDO	SL	DRAIN			1GD
176	5	40	CWDO	SL	DRAIN	NOT		1GD
190	5	100	CWDO	SLFD	RECON			100G
191	5	100	DH20	SLFD	RECON			100G

LOG OF SETTLING VESSELS ACCORDING TO #, COMPOSITION AND TREATMENT

SV#	SL from	NomSL Conc.	DIL.	So Type	Treat 1	Treat 2	Treat 3	SV Type
14	1	40	CWDO	WSL	DIL			100G
15	1	20	CWDO	WSL	DIL			100G
21	4	40	CWDO	SL	DIL			PS
22	4	20	CWDO	SL	DIL			PS
23	4	10	CWDO	SL	DIL			PSS
24	4	5	CWDO	SL	DIL			PS
25	4	40	CWDO	SL	AL	5000		100G
26	4	40	CWDO	SL	AL	3000		100G
27	4	40	CWDO	SL	AL	2000		100G
28	4	40	CWDO	SL	AL	1000		100G
29	4	40	CWDO	SL	AL	500		100G
58	1	100	CWDO	I	RECON			PS
59	1	60	CWDO	I	RECON	DIL		PS
60	1	40	CWDO	I	RECON	DIL		PS
61	1	20	CWDO	I	RECON	DIL		PS
63	1	100	CWDO	II	RECON			PS
64	1	60	CWDO	II	RECON	DIL		PS
65	1	40	CWDO	II	RECON	DIL		PS
66	1	20	CWDO	II	RECON	DIL		PS
68	1	100	CWDO	III	RECON			PS
68A	1	100	CWDO	III	FRTH			PS
68B	1	100	CWDO	III	FRTH	REH20		PS
69	1	60	CWDO	III	RECON	DIL		PS
70	1	40	CWDO	III	RECON	DIL		PS
71	1	20	CWDO	III	RECON	DIL		PS
72	1	5	CWDO	III	RECON	DIL		PS
87	4	40	CWDO	SL	AL	250		100G
88	4	40	CWDO	SL	AL	150		100G
89	4	40	CWDO	SL	AL	100		100G
90	4	40	CWDO	SL	AL	50		100G
[illegible]	4	40	CWDO	SL	FRTH			PS
[illegible]	4	20	CWDO	SL	FRTH			PS
[illegible]	4	40	CWDO	SL	FRTH			PS
106	4	60	CWDO	SL	FRTH			PS
107	4	80	CWDO	SL	FRTH			PS
115	1	100	CWDO	SLEA	RECON			100G
141	4	0	CWDO		AL			100G
145	4	40	CWDO	SL	DRAIN			5GD
146	4	40	CWDO	SL	DRAIN			5GD
147	4	40	CWDO	SL	DRAIN			1GD
148	1	40	CWDO	SL	DRAIN			1GD
151	1	40	CWDO	III	RECON	DIL		100G
152	1	40	CWDO	III	RECON	DIL	NAOH	100G
152A	1	40	CWDO	III	REH20	RESET		
175	5	40	CWDO	SL	DRAIN			1GD
176	5	40	CWDO	SL	DRAIN	NOT		1GD
190	5	100	CWDO	SLFD	RECON			100G
1	1	80	CWF	WSL	DIL			1G
2	1	60	CWF	WSL	DIL			1G
3	1	40	CWF	WSL	DIL			100G
4	1	20	CWF	WSL	DIL			100G
5	1	5	CWF	WSL	DIL			100G
6	1	50	CWF	WSL	DIL			100G

EXPLOGDIL (MR).2

[illegible] OF TESTING VESSELS ACCORDING TO #,COMPOSITION AND TREATMENT

SV#	SL from	NomSL Conc.	DIL.	Soil Type	Treat 1	Treat 2	Treat 3	SV Type
7	1	40	CWF	WSL	DIL			100G
8	1	30	CWF	WSL	DIL			100G
9	1	20	CWF	WSL	DIL			100G
10	1	10	CWF	WSL	DIL			100G
11	1	5	CWF	WSL	DIL			100G
18	1	40	CWF	WSL	AL			100G
126	4	60	DH20	SLL	DIL	HCL		100G
16	1	40	DH20	WSL	DIL			100G
17	1	20	DH20	WSL	DIL			100G
35	4	40	DH20	SL	DEOIL	F1REM		PS
36	4	40	DH20	SL	DEOIL	F2REM		PS
37	4	40	DH20	SL	DEOIL	F3REM		PS
38	4	40	DH20	SL	DEOIL	DEK		250G
42	4	40	DH20	SL	DEOIL	STIR		PS
43	1	100	DH20	I	RECON			PS
44	1	60	DH20	I	RECON	DIL		PS
45	1	40	DH20	I	RECON	DIL		PS
46	1	20	DH20	I	RECON	DIL		PS
47	1	5	DH20	I	RECON	DIL		PS
48	1	100	DH20	II	RECON			PS
49	1	60	DH20	II	RECON	DIL		PS
50	1	40	DH20	II	RECON	DIL		PS
51	1	20	DH20	II	RECON	DIL		PS
52	1	5	DH20	II	RECON	DIL		PS
53	1	100	DH20	III	RECON			PS
53A	1	100	DH20	III	FRTH			PS
53B	1	100	DH20	III	FRTH	REH20		PS
54	1	60	DH20	III	RECON	DIL		PS
55	1	40	DH20	III	RECON	DIL		PS
56	1	20	DH20	III	RECON	DIL		PS
56A	1	[illegible]	DH20	III	REH20	RESET		PS
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]
[illegible]	[illegible]	[illegible]	DH20	III	RECON	DIL		PS
73A	1	15	DH20	III	REH20	RESET		PS
74	1	10	DH20	III	RECON	DIL		PS
75	4	40	DH20	SL	DEOIL	STIR		100G
76	4	40	DH20	SL	DEOIL	STIR		PS
77	4	40	DH20	SL	DEOIL	F1REM		100G
78	4	40	DH20	SL	DEOIL	F2REM		100G
79	4	40	DH20	SL	DEOIL	F3REM		100G
80	4	40	DH20	SL	DEOIL	DEK		250G
81	4	40	DH20	SL	DEOIL	DEK	HCL	250G
91	4	40	DH20	DEC	UF			100G
95	4	40	DH20	SL	FRTH			PS
96	4	40	DH20	DEC	FRTH	UF		PS
97	4	40	DH20	SED	DEK			100G
98	1	100	DH20	SLE	SWEL			100G
99	1	100	DH20	CSOD	SWEL			100G
100	1	100	DH20	I	SWEL			100G
101	1	100	DH20	III	FER	AMREM	RECON	100G
102	1	100	DH20	SLE	RECON			100G
103	1	100	DH20	CSOD	RECON			100G
114	1	100	DH20	SLEA	RECON			100G

EXPLOGDIL (MR).3

LOG OF SETTLING VESSELS ACCORDING TO #,COMPOSITION AND TREATMENT

SV#	SL from	NomSL Conc.	DIL.	Sol Type	Treat 1	Treat 2	Treat 3	SV Type
116	4	60	DH20	SL	FER	SA	SFC5	100G
117	4	60	DH20	SL	FER	SA	SFC10	100G
118	4	60	DH20	SL	FER	SA	ACC5	100G
119	4	60	DH20	SL	FER	SA	ACC10	100G
120	1	100	DH20	III	RECON	HEAT		100G
121	4	60	DH20	SLL	FER	SA	SFC20	100G
122	4	60	DH20	SLL	FER	SA	SFC40	100G
123	4	60	DH20	SLL	FER	SA	ACC20	100G
124	4	60	DH20	SLL	FER	SA	ACC40	100G
125	4	60	DH20	SLL	DIL			100G
131	BE	5	DH20	ST	NONE			1G
135	BE	80	DH20	ST	COMP			100G
135B	BE	80	DH20	ST	FRTH	COMP		PS
149	1	40	DH20	DEC	AL			250G
158	1	40	DH20	III	RECON	DIL	NAOH	100G
160	5	20	DH20	SL	DIL			1MG
161	5	40	DH20	SL	DRAIN			500GD
191	5	100	DH20	SLFD	RECON			100G
155	5	40	H202	SL	DIL			100G
156	5	40	H202	SL	DIL	STIR		100G
113	4	40	HCL	SL	FER	AWASH		100G
140	4	100	HCL	III	FER	AWASH	RECON	100G
82	1	100	MEOH	II	RECON			PS
83	1	60	MEOH	II	RECON	DIL		PS
84	1	40	MEOH	II	RECON	DIL		PS
85	1	20	MEOH	II	RECON	DIL		PS
86	1	5	MEOH	II	RECON	DIL		PS
139	1	100	MEOH	II	RECON	REH20		100G
139B	1	100	MEOH	II	FRTH			PS
129	4	40	NAOH	SL	DIL	.1N		100G
129A	4	40	NAOH	SL	REH20	RESET		
[illegible]	[illegible]	[illegible]	[illegible]	SL	DIL	[illegible]		100G
132	BE	5	NAOH	ST	NONE	.01%		1G
133	BE	5	NAOH	ST	NONE	.02%		1G
133AL	BE	5	NAOH	ST	AL	DEKC		250G
133ALR	BE	5	NAOH	ST	AL	DEKC		250G
133FE	BE	5	NAOH	ST	FE	DEKC		250G
134	BE	5	NAOH	ST	NONE	.04%		1G
134AL	BE	5	NAOH	ST	AL	DEKC		250G
136	BE	80	NAOH	ST	COMP			100G
136B	BE	80	NAOH	ST	FRTH	COMP		PS
137	1	100	NAOH	II	RECON	REH20		100G
137B	1	100	NAOH	II	FRTH			PS
138	1	100	NAOH	III	RECON	REH20		100G
138B	1	100	NAOH	III	FRTH			PS
153	5	40	NAOH	SL	DIL			100G
154	5	40	NAOH	SL	DIL	STIR		100G
157	5	0	NAOH	CWDO	DIL			100G
159	1	100	NAOH	SLE	RECON	REH20		100G
162	5	100	NAOH	SLFD	RECON	REH20		100G
A	1	100	NONE	WSL	NONE			2MG
12	2	100	NONE	WSL	NONE			1G
13	2	100	NONE	WSL	VIBES			1G

LOG OF SETTLING VESSELS ACCORDING TO #,COMPOSITION AND TREATMENT

SV#	SL from	NomSL Conc.	DIL.	Soil Type	Treat 1	Treat 2	Treat 3	SV Type
18A	1	100	NONE	WSL	AL			100G
19	1	100	NONE	SL	NONE			PS
19A	1	100	NONE	SL	FRTH			PS
19B	1	100	NONE	SL	FRTH			PS
30	4	100	NONE	SL	FRTH	STIR		100G
39	4	100	NONE	SL	DEOIL	F1REM		PS
40	4	100	NONE	SL	DEOIL	F2REM		PS
41	4	100	NONE	SL	DEOIL	F3REM		PS
92	4	100	NONE	SL	FRTH			PS
93	4	100	NONE	SL	FRTH			PS
108	4	100	NONE	SL	FRTH			PS
109	2	127	NONE	WSL	FRTH	COMP		PS
110	2	143	NONE	WSL	FRTH	COMP		PS
111	2	178	NONE	WSL	FRTH	COMP		PS
112	2	234	NONE	WSL	FRTH	COMP		PS
127	4	100	NONE	SL	HEAT			100G
128	4	100	NONE	SL	HEAT	HCL		100G
142	4	100	NONE	SL	NONE			1G
143	4	100	NONE	SL	NONE			TLC
144	4	100	NONE	SL	NONE			TLC
150	5	100	NONE	SL	AL			100G

LOG OF SETTLING VESSELS ACCORDING TO #, COMPOSITION AND TREATMENT

SV#	SL from	NomSL Conc.	DIL.	Sol Type	Treat 1	Treat 2	Treat 3	SV Type
112	2	234	NONE	WSL	FRTH	COMP		PS
111	2	178	NONE	WSL	FRTH	COMP		PS
110	2	143	NONE	WSL	FRTH	COMP		PS
109	2	127	NONE	WSL	FRTH	COMP		PS
99	1	100	DH20	CSOD	SWEL			100G
103	1	100	DH20	CSOD	RECON			100G
43	1	100	DH20	I	RECON			PS
58	1	100	CWDO	I	RECON			PS
100	1	100	DH20	I	SWEL			100G
48	1	100	DH20	II	RECON			PS
63	1	100	CWDO	II	RECON			PS
82	1	100	MEOH	II	RECON			PS
137	1	100	NAOH	II	RECON	REH20		100G
137B	1	100	NAOH	II	FRTH			PS
139	1	100	MEOH	II	RECON	REH20		100G
139B	1	100	MEOH	II	FRTH			PS
53	1	100	DH20	III	RECON			PS
53A	1	100	DH20	III	FRTH			PS
53B	1	100	DH20	III	FRTH	REH20		PS
68	1	100	CWDO	III	RECON			PS
68A	1	100	CWDO	III	FRTH			PS
68B	1	100	CWDO	III	FRTH	REH20		PS
101	1	100	DH20	III	FER	AMREM	RECON	100G
120	1	100	DH20	III	RECON	HEAT		100G
138	1	100	NAOH	III	RECON	REH20		100G
138B	1	100	NAOH	III	FRTH			PS
140	4	100	HCL	III	FER	AWASH	RECON	100G
19	1	100	NONE	SL	NONE			PS
19A	1	100	NONE	SL	FRTH			PS
19B	1	100	NONE	SL	FRTH			PS
[illegible]	4	100	NONE	SL	FRTH	STIR		100G
[illegible]	4	100	NONE	SL	[illegible]	[illegible]		PS
[illegible]	4	100	NONE	SL	DEOIL	F3REM		PS
41	4	100	NONE	SL	DEOIL	F3REM		PS
92	4	100	NONE	SL	FRTH			PS
93	4	100	NONE	SL	FRTH			PS
108	4	100	NONE	SL	FRTH			PS
127	4	100	NONE	SL	HEAT			100G
[illegible]	4	100	NONE	SL	HEAT	HCL		100G
[illegible]	4	100	NONE	SL	NONE			1G
143	4	100	NONE	SL	NONE			TLC
144	4	100	NONE	SL	NONE			TLC
150	5	100	NONE	SL	AL			100G
98	1	100	DH20	SLE	SWEL			100G
102	1	100	DH20	SLE	RECON			100G
159	1	100	NAOH	SLE	RECON	REH20		100G
114	1	100	DH20	SLEA	RECON			100G
115	1	100	CWDO	SLEA	RECON			100G
162	5	100	NAOH	SLFD	RECON	REH20		100G
190	5	100	CWDO	SLFD	RECON			100G
191	5	100	DH20	SLFD	RECON			100G
A	1	100	NONE	WSL	NONE			2MG
12	2	100	NONE	WSL	NONE			1G

LOG OF SETTLING VESSELS ACCORDING TO #,COMPOSITION AND TREATMENT

SV#	SL from	NomSL Conc.	DIL.	Soil Type	Treat 1	Treat 2	Treat 3	SV Type
13	2	100	NONE	WSL	VIBES			1G
18A	1	100	NONE	WSL	AL			100G
107	4	80	CWDO	SL	FRTH			PS
135	BE	80	DH20	ST	COMP			100G
135B	BE	80	DH20	ST	FRTH	COMP		PS
136	BE	80	NAOH	ST	COMP			100G
136B	BE	80	NAOH	ST	FRTH	COMP		PS
1	1	80	CWF	WSL	DIL			1G
44	1	60	DH20	I	RECON	DIL		PS
59	1	60	CWDO	I	RECON	DIL		PS
49	1	60	DH20	II	RECON	DIL		PS
64	1	60	CWDO	II	RECON	DIL		PS
83	1	60	MEOH	II	RECON	DIL		PS
54	1	60	DH20	III	RECON	DIL		PS
69	1	60	CWDO	III	RECON	DIL		PS
106	4	60	CWDO	SL	FRTH			PS
116	4	60	DH20	SL	FER	SA	SFC5	100G
117	4	60	DH20	SL	FER	SA	SFC10	100G
118	4	60	DH20	SL	FER	SA	ACC5	100G
119	4	60	DH20	SL	FER	SA	ACC10	100G
121	4	60	DH20	SLL	FER	SA	SFC20	100G
122	4	60	DH20	SLL	FER	SA	SFC40	100G
123	4	60	DH20	SLL	FER	SA	ACC20	100G
124	4	60	DH20	SLL	FER	SA	ACC40	100G
125	4	60	DH20	SLL	DIL			100G
126	4	60	DH20	SLL	DIL	HCL		100G
2	1	60	CWF	WSL	DIL			1G
6	1	50	CWF	WSL	DIL			100G
91	4	40	DH20	DEC	UF			100G
96	4	40	DH20	DEC	FRTH	UF		PS
149	1	40	DH20	DEC	AL			250G
[illegible]	[illegible]	40	[illegible]	I	RECON	DIL		[illegible]
[illegible]	1	40	CWDO	I	RECON	DIL		PS
50	1	40	DH20	II	RECON	DIL		PS
65	1	40	CWDO	II	RECON	DIL		PS
84	1	40	MEOH	II	RECON	DIL		PS
55	1	40	DH20	III	RECON	DIL		PS
70	1	40	CWDO	III	RECON	DIL		PS
151	1	40	CWDO	III	RECON	DIL		100G
152	1	40	CWDO	III	RECON	DIL	NAOH	100G
152A	1	40	CWDO	III	REH20	RESET		
158	1	40	DH20	III	RECON	DIL	NAOH	100G
97	4	40	DH20	SED	DEK			100G
21	4	40	CWDO	SL	DIL			PS
25	4	40	CWDO	SL	AL	5000		100G
26	4	40	CWDO	SL	AL	3000		100G
27	4	40	CWDO	SL	AL	2000		100G
28	4	40	CWDO	SL	AL	1000		100G
29	4	40	CWDO	SL	AL	500		100G
35	4	40	DH20	SL	DEOIL	F1REM		PS
36	4	40	DH20	SL	DEOIL	F2REM		PS
37	4	40	DH20	SL	DEOIL	F3REM		PS
38	4	40	DH20	SL	DEOIL	DEK		250G

LOG OF SETTLING VESSELS ACCORDING TO #,COMPOSITION AND TREATMENT

SV#	SL from	NomSL Conc.	DIL	Sol Type	Treat 1	Treat 2	Treat 3	SV Type
42	4	40	DH20	SL	DEOIL	STIR		PS
75	4	40	DH20	SL	DEOIL	STIR		100G
76	4	40	DH20	SL	DEOIL	STIR		PS
77	4	40	DH20	SL	DEOIL	F1REM		100G
78	4	40	DH20	SL	DEOIL	F2REM		100G
79	4	40	DH20	SL	DEOIL	F3REM		100G
80	4	40	DH20	SL	DEOIL	DEK		250G
81	4	40	DH20	SL	DEOIL	DEK	HCL	250G
87	4	40	CWDO	SL	AL	250		100G
88	4	40	CWDO	SL	AL	150		100G
89	4	40	CWDO	SL	AL	100		100G
90	4	40	CWDO	SL	AL	50		100G
94	4	40	CWDO	SL	FRTH			PS
95	4	40	DH20	SL	FRTH			PS
105	4	40	CWDO	SL	FRTH			PS
113	4	40	HCL	SL	FER	AWASH		100G
129	4	40	NAOH	SL	DIL	.1N		100G
129A	4	40	NAOH	SL	REH20	RESET		
130	4	40	NAOH	SL	DIL	.01N		100G
145	4	40	CWDO	SL	DRAIN			5GD
146	4	40	CWDO	SL	DRAIN			5GD
147	4	40	CWDO	SL	DRAIN			1GD
148	1	40	CWDO	SL	DRAIN			1GD
153	5	40	NAOH	SL	DIL			100G
154	5	40	NAOH	SL	DIL	STIR		100G
155	5	40	H202	SL	DIL			100G
156	5	40	H202	SL	DIL	STIR		100G
161	5	40	DH20	SL	DRAIN			500GD
175	5	40	CWDO	SL	DRAIN			1GD
176	5	40	CWDO	SL	DRAIN	NOT		1GD
3	1	40	CWF	WSL	DIL			100G
[illegible]	[illegible]	40	CWF	WSL	DIL			100G
14	1	40	CWDO	WSL	DIL			100G
16	1	40	DH20	WSL	DIL			100G
18	1	40	CWF	WSL	AL			100G
8	1	30	CWF	WSL	DIL			100G
46	1	20	DH20	I	RECON	DIL		PS
61	1	20	CWDO	I	RECON	DIL		PS
51	1	20	DH20	II	RECON	DIL		PS
55	1	20	CWDO	II	RECON	DIL		PS
85	1	20	MEOH	II	RECON	DIL		PS
56	1	20	DH20	III	RECON	DIL		PS
56A	1	20	DH20	III	REH20	RESET		PS
71	1	20	CWDO	III	RECON	DIL		PS
22	4	20	CWDO	SL	DIL			PS
104	4	20	CWDO	SL	FRTH			PS
160	5	20	DH20	SL	DIL			1MG
4	1	20	CWF	WSL	DIL			100G
9	1	20	CWF	WSL	DIL			100G
15	1	20	CWDO	WSL	DIL			100G
17	1	20	DH20	WSL	DIL			100G
73	1	15	DH20	III	RECON	DIL		PS
73A	1	15	DH20	III	REH20	RESET		PS

LOG OF SETTLING VESSELS ACCORDING TO #,COMPOSITION AND TREATMENT

SV#	SL from	NomSL Conc.	DIL	Sol Type	Treat 1	Treat 2	Treat 3	SV Type
74	1	10	DH20	III	RECON	DIL		PS
23	4	10	CWDO	SL	DIL			PSS
10	1	10	CWF	WSL	DIL			100G
47	1	5	DH20	I	RECON	DIL		PS
52	1	5	DH20	II	RECON	DIL		PS
86	1	5	MEOH	II	RECON	DIL		PS
57	1	5	DH20	III	RECON	DIL		PS
72	1	5	CWDO	III	RECON	DIL		PS
24	4	5	CWDO	SL	DIL			PS
131	BE	5	DH20	ST	NONE			1G
132	BE	5	NAOH	ST	NONE	.01%		1G
133	BE	5	NAOH	ST	NONE	.02%		1G
133AL	BE	5	NAOH	ST	AL	DEKC		250G
133ALR	BE	5	NAOH	ST	AL	DEKC		250G
133FE	BE	5	NAOH	ST	FE	DEKC		250G
134	BE	5	NAOH	ST	NONE	.04%		1G
134AL	BE	5	NAOH	ST	AL	DEKC		250G
5	1	5	CWF	WSL	DIL			100G
11	1	5	CWF	WSL	DIL			100G
157	5	0	NAOH	CWDO	DIL			100G
141	4	0	CWDO		AL			100G

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                                                              EXPLOGSOL (MR).1
   LOG OF SETTLING VESSELS ACCORDING TO #,COMPOSITION AND TREATMENT

      SV#       SL    NomSL   DIL.   Sol    Treat   Treat   Treat   SV
                from  Conc.          Type   1       2       3       Type
   --------------------------------------------------------------------------
         99      1     100   DH20   CSOD   SWEL                     100G
        103      1     100   DH20   CSOD   RECON                    100G
        157      5       0   NAOH   CWDO   DIL                      100G
         91      4      40   DH20   DEC    UF                       100G
         96      4      40   DH20   DEC    FRTH    UF               PS
        149      1      40   DH20   DEC    AL                       250G
         43      1     100   DH20   I      RECON                    PS
         44      1      60   DH20   I      RECON   DIL              PS
         45      1      40   DH20   I      RECON   DIL              PS
         46      1      20   DH20   I      RECON   DIL              PS
         47      1       5   DH20   I      RECON   DIL              PS
         58      1     100   CWDO   I      RECON                    PS
         59      1      60   CWDO   I      RECON   DIL              PS
         60      1      40   CWDO   I      RECON   DIL              PS
         61      1      20   CWDO   I      RECON   DIL              PS
        100      1     100   DH20   I      SWEL                     100G
         48      1     100   DH20   II     RECON                    PS
         49      1      60   DH20   II     RECON   DIL              PS
         50      1      40   DH20   II     RECON   DIL              PS
         51      1      20   DH20   II     RECON   DIL              PS
         52      1       5   DH20   II     RECON   DIL              PS
         63      1     100   CWDO   II     RECON                    PS
         64      1      60   CWDO   II     RECON   DIL              PS
         65      1      40   CWDO   II     RECON   DIL              PS
         66      1      20   CWDO   II     RECON   DIL              PS
         82      1     100   MEOH   II     RECON                    PS
         83      1      60   MEOH   II     RECON   DIL              PS
         84      1      40   MEOH   II     RECON   DIL              PS
         85      1      20   MEOH   II     RECON   DIL              PS
         86      1       5   MEOH   II     RECON   DIL              PS
        137      1     100   NAOH   II     RECON   REH20            100G
   [illegible]   1     100   NAOH   II     FRTH                     PS
   [illegible]   1     100   MEOH   II     RECON   REH20            100G
   139B          1     100   MEOH   II     FRTH                     PS
         53      1     100   DH20   III    RECON                    PS
   53A           1     100   DH20   III    FRTH                     PS
   53B           1     100   DH20   III    FRTH    REH20            PS
         54      1      60   DH20   III    RECON   DIL              PS
         55      1      40   DH20   III    RECON   DIL              PS
         56      1      20   DH20   III    RECON   DIL              PS
   56A           1      20   DH20   III    REH20   RESET            PS
         57      1       5   DH20   III    RECON   DIL              PS
         68      1     100   CWDO   III    RECON                    PS
   68A           1     100   CWDO   III    FRTH                     PS
   68B           1     100   CWDO   III    FRTH    REH20            PS
         69      1      60   CWDO   III    RECON   DIL              PS
         70      1      40   CWDO   III    RECON   DIL              PS
         71      1      20   CWDO   III    RECON   DIL              PS
         72      1       5   CWDO   III    RECON   DIL              PS
         73      1      15   DH20   III    RECON   DIL              PS
   73A           1      15   DH20   III    REH20   RESET            PS
         74      1      10   DH20   III    RECON   DIL              PS
        101      1     100   DH20   III    FER     AMREM   RECON    100G
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LOG OF SETTLING VESSELS ACCORDING TO #,COMPOSITION AND TREATMENT

SV#	SL from	NomSL Conc.	DIL.	Sol Type	Treat 1	Treat 2	Treat 3	SV Type
120	1	100	DH20	III	RECON	HEAT		100G
138	1	100	NAOH	III	RECON	REH20		100G
138B	1	100	NAOH	III	FRTH			PS
140	4	100	HCL	III	FER	AWASH	RECON	100G
151	1	40	CWDO	III	RECON	DIL		100G
152	1	40	CWDO	III	RECON	DIL	NAOH	100G
152A	1	40	CWDO	III	REH20	RESET		
158	1	40	DH20	III	RECON	DIL	NAOH	100G
97	4	40	DH20	SED	DEK			100G
19	1	100	NONE	SL	NONE			PS
19A	1	100	NONE	SL	FRTH			PS
19B	1	100	NONE	SL	FRTH			PS
21	4	40	CWDO	SL	DIL			PS
22	4	20	CWDO	SL	DIL			PS
23	4	10	CWDO	SL	DIL			PSS
24	4	5	CWDO	SL	DIL			PS
25	4	40	CWDO	SL	AL	5000		100G
26	4	40	CWDO	SL	AL	3000		100G
27	4	40	CWDO	SL	AL	2000		100G
28	4	40	CWDO	SL	AL	1000		100G
29	4	40	CWDO	SL	AL	500		100G
30	4	100	NONE	SL	FRTH	STIR		100G
35	4	40	DH20	SL	DEOIL	F1REM		PS
36	4	40	DH20	SL	DEOIL	F2REM		PS
37	4	40	DH20	SL	DEOIL	F3REM		PS
38	4	40	DH20	SL	DEOIL	DEK		250G
39	4	100	NONE	SL	DEOIL	F1REM		PS
40	4	100	NONE	SL	DEOIL	F2REM		PS
41	4	100	NONE	SL	DEOIL	F3REM		PS
42	4	40	DH20	SL	DEOIL	STIR		PS
75	4	40	DH20	SL	DEOIL	STIR		100G
76	4	40	DH20	SL	DEOIL	STIR		PS
77	4	40	DH20	SL	DEOIL	F1REM		100G
78	4	40	DH20	SL	DEOIL	F2REM		100G
79	4	40	DH20	SL	DEOIL	F3REM		100G
80	4	40	DH20	SL	DEOIL	DEK		250G
81	4	40	DH20	SL	DEOIL	DEK	HCL	250G
87	4	40	CWDO	SL	AL	250		100G
88	4	40	CWDO	SL	AL	150		100G
89	4	40	CWDO	SL	AL	100		100G
90	4	40	CWDO	SL	AL	50		100G
92	4	100	NONE	SL	FRTH			PS
93	4	100	NONE	SL	FRTH			PS
94	4	40	CWDO	SL	FRTH			PS
95	4	40	DH20	SL	FRTH			PS
104	4	20	CWDO	SL	FRTH			PS
105	4	40	CWDO	SL	FRTH			PS
106	4	60	CWDO	SL	FRTH			PS
107	4	80	CWDO	SL	FRTH			PS
108	4	100	NONE	SL	FRTH			PS
113	4	40	HCL	SL	FER	AWASH		100G
116	4	60	DH20	SL	FER	SA	SFC5	100G
117	4	60	DH20	SL	FER	SA	SFC10	100G

LOG OF SETTLING VESSELS ACCORDING TO #, COMPOSITION AND TREATMENT

SV#	SL from	NomSL Conc.	DIL.	Sol Type	Treat 1	Treat 2	Treat 3	SV Type
118	4	60	DH20	SL	FER	SA	ACC5	100G
119	4	60	DH20	SL	FER	SA	ACC10	100G
127	4	100	NONE	SL	HEAT			100G
128	4	100	NONE	SL	HEAT	HCL		100G
129	4	40	NAOH	SL	DIL	.1N		100G
129A	4	40	NAOH	SL	REH20	RESET		
130	4	40	NAOH	SL	DIL	.01N		100G
142	4	100	NONE	SL	NONE			1G
143	4	100	NONE	SL	NONE			TLC
144	4	100	NONE	SL	NONE			TLC
145	4	40	CWDO	SL	DRAIN			5GD
146	4	40	CWDO	SL	DRAIN			5GD
147	4	40	CWDO	SL	DRAIN			1GD
148	1	40	CWDO	SL	DRAIN			1GD
150	5	100	NONE	SL	AL			100G
153	5	40	NAOH	SL	DIL			100G
154	5	40	NAOH	SL	DIL	STIR		100G
155	5	40	H202	SL	DIL			100G
156	5	40	H202	SL	DIL	STIR		100G
160	5	20	DH20	SL	DIL			1MG
161	5	40	DH20	SL	DRAIN			500GD
175	5	40	CWDO	SL	DRAIN			1GD
176	5	40	CWDO	SL	DRAIN	NOT		1GD
98	1	100	DH20	SLE	SWEL			100G
102	1	100	DH20	SLE	RECON			100G
159	1	100	NAOH	SLE	RECON	REH20		100G
114	1	100	DH20	SLEA	RECON			100G
115	1	100	CWDO	SLEA	RECON			100G
162	5	100	NAOH	SLFD	RECON	REH20		100G
190	5	100	CWDO	SLFD	RECON			100G
191	5	100	DH20	SLFD	RECON			100G
121	4	60	DH20	SLL	FER	SA	[illegible]	100G
122	4	60	DH20	SLL	FER	SA	EFC40	100G
123	4	60	DH20	SLL	FER	SA	ACC20	100G
124	4	60	DH20	SLL	FER	SA	ACC40	100G
125	4	60	DH20	SLL	DIL			100G
126	4	60	DH20	SLL	DIL	HCL		100G
131	BE	5	DH20	ST	NONE			1G
132	BE	5	NAOH	ST	NONE	.01%		1G
133	BE	5	NAOH	ST	NONE	.02%		1G
133AL	BE	5	NAOH	ST	AL	DEKC		250G
133ALR	BE	5	NAOH	ST	AL	DEKC		250G
133FE	BE	5	NAOH	ST	FE	DEKC		250G
134	BE	5	NAOH	ST	NONE	.04%		1G
134AL	BE	5	NAOH	ST	AL	DEKC		250G
135	BE	80	DH20	ST	COMP			100G
135B	BE	80	DH20	ST	FRTH	COMP		PS
136	BE	80	NAOH	ST	COMP			100G
136B	BE	80	NAOH	ST	FRTH	COMP		PS
A	1	100	NONE	WSL	NONE			2MG
1	1	80	CWF	WSL	DIL			1G
2	1	60	CWF	WSL	DIL			1G
3	1	40	CWF	WSL	DIL			100G

LOG OF SETTLING VESSELS ACCORDING TO #,COMPOSITION AND TREATMENT

SV#	SL from	NomSL Conc.	DIL.	Sol Type	Treat 1	Treat 2	Treat 3	SV Type
4	1	20	CWF	WSL	DIL			100G
5	1	5	CWF	WSL	DIL			100G
6	1	50	CWF	WSL	DIL			100G
7	1	40	CWF	WSL	DIL			100G
8	1	30	CWF	WSL	DIL			100G
9	1	20	CWF	WSL	DIL			100G
10	1	10	CWF	WSL	DIL			100G
11	1	5	CWF	WSL	DIL			100G
12	2	100	NONE	WSL	NONE			1G
13	2	100	NONE	WSL	VIBES			1G
14	1	40	CWDO	WSL	DIL			100G
15	1	20	CWDO	WSL	DIL			100G
16	1	40	DH20	WSL	DIL			100G
17	1	20	DH20	WSL	DIL			100G
18	1	40	CWF	WSL	AL			100G
18A	1	100	NONE	WSL	AL			100G
109	2	127	NONE	WSL	FRTH	COMP		PS
110	2	143	NONE	WSL	FRTH	COMP		PS
111	2	178	NONE	WSL	FRTH	COMP		PS
112	2	234	NONE	WSL	FRTH	COMP		PS
141	4	0	CWDO		AL			100G

LOG OF SETTLING VESSELS ACCORDING TO =,COMPOSITION AND TREATMENT

SV#	SL from	NomSL Conc	DIL.	Sol Type	Treat 1	Treat 2	Treat 3	SV Type
149	1	40	DH20	DEC	AL			250G
25	4	40	CWDO	SL	AL	5000		100G
26	4	40	CWDO	SL	AL	3000		100G
27	4	40	CWDO	SL	AL	2000		100G
28	4	40	CWDO	SL	AL	1000		100G
29	4	40	CWDO	SL	AL	500		100G
87	4	40	CWDO	SL	AL	250		100G
88	4	40	CWDO	SL	AL	150		100G
89	4	40	CWDO	SL	AL	100		100G
90	4	40	CWDO	SL	AL	50		100G
150	5	100	NONE	SL	AL			100G
133AL	BE	5	NAOH	ST	AL	DEKC		250G
133ALR	BE	5	NAOH	ST	AL	DEKC		250G
134AL	BE	5	NAOH	ST	AL	DEKC		250G
18	1	40	CWF	WSL	AL			100G
18A	1	100	NONE	WSL	AL			100G
141	4	0	CWDO		AL			100G
135	BE	80	DH20	ST	COMP			100G
136	BE	80	NAOH	ST	COMP			100G
97	4	40	DH20	SED	DEK			100G
35	4	40	DH20	SL	DEOIL	F1REM		PS
36	4	40	DH20	SL	DEOIL	F2REM		PS
37	4	40	DH20	SL	DEOIL	F3REM		PS
38	4	40	DH20	SL	DEOIL	DEK		250G
39	4	100	NONE	SL	DEOIL	F1REM		PS
40	4	100	NONE	SL	DEOIL	F2REM		PS
41	4	100	NONE	SL	DEOIL	F3REM		PS
42	4	40	DH20	SL	DEOIL	STIR		PS
75	4	40	DH20	SL	DEOIL	STIR		100G
76	4	40	DH20	SL	DEOIL	STIR		PS
77	4	40	DH20	SL	DEOIL	F1REM		100G
78	4	40	DH20	SL	DEOIL	F2REM		100G
79	4	40	DH20	SL	DEOIL	F3REM		100G
80	4	40	DH20	SL	DEOIL	DEK		250G
81	4	40	DH20	SL	DEOIL	DEK	HCL	250G
157	5	0	NAOH	CWDO	DIL			100G
21	4	40	CWDO	SL	DIL			PS
22	4	20	CWDO	SL	DIL			PS
23	4	10	CWDO	SL	DIL			PSS
24	4	5	CWDO	SL	DIL			PS
129	4	40	NAOH	SL	DIL	.1N		100G
130	4	40	NAOH	SL	DIL	.01N		100G
153	5	40	NAOH	SL	DIL			100G
154	5	40	NAOH	SL	DIL	STIR		100G
155	5	40	H202	SL	DIL			100G
156	5	40	H202	SL	DIL	STIR		100G
160	5	20	DH20	SL	DIL			1MG
125	4	60	DH20	SLL	DIL			100G
126	4	60	DH20	SLL	DIL	HCL		100G
1	1	80	CWF	WSL	DIL			1G
2	1	60	CWF	WSL	DIL			1G
3	1	40	CWF	WSL	DIL			100G
4	1	20	CWF	WSL	DIL			100G

EXPLOGTREAT (MR).2

LOG OF SETTLING VESSELS ACCORDING TO #,COMPOSITION AND TREATMENT

SV#	SL From	NomSL Conc.	DIL.	Soil Type	Treat 1	Treat 2	Treat 3	SV Type
5	1	5	CWF	WSL	DIL			100G
6	1	50	CWF	WSL	DIL			100G
7	1	40	CWF	WSL	DIL			100G
8	1	30	CWF	WSL	DIL			100G
9	1	20	CWF	WSL	DIL			100G
10	1	10	CWF	WSL	DIL			100G
11	1	5	CWF	WSL	DIL			100G
14	1	40	CWDO	WSL	DIL			100G
15	1	20	CWDO	WSL	DIL			100G
16	1	40	DH20	WSL	DIL			100G
17	1	20	DH20	WSL	DIL			100G
145	4	40	CWDO	SL	DRAIN			5GD
146	4	40	CWDO	SL	DRAIN			5GD
147	4	40	CWDO	SL	DRAIN			1GD
148	1	40	CWDO	SL	DRAIN			1GD
161	5	40	DH20	SL	DRAIN			500GD
175	5	40	CWDO	SL	DRAIN			1GD
176	5	40	CWDO	SL	DRAIN	NOT		1GD
133FE	BE	5	NAOH	ST	FE	DEKC		250G
101	1	100	DH20	III	FER	AMREM	RECON	100G
140	4	100	HCL	III	FER	AWASH	RECON	100G
113	4	40	HCL	SL	FER	AWASH		100G
116	4	60	DH20	SL	FER	SA	SFC5	100G
117	4	60	DH20	SL	FER	SA	SFC10	100G
118	4	60	DH20	SL	FER	SA	ACC5	100G
119	4	60	DH20	SL	FER	SA	ACC10	100G
121	4	60	DH20	SLL	FER	SA	SFC20	100G
122	4	60	DH20	SLL	FER	SA	SFC40	100G
123	4	60	DH20	SLL	FER	SA	ACC20	100G
124	4	60	DH20	SLL	FER	SA	ACC40	100G
[illegible]	4	40	DH20	DEC	FRTH	[illegible]		PS
[illegible]	[illegible]	100	NAOH	II	FRTH			PS
[illegible]	[illegible]	100	MEOH	II	FRTH			PS
53A	1	100	DH20	III	FRTH			PS
53B	1	100	DH20	III	FRTH	REH20		PS
68A	1	100	CWDO	III	FRTH			PS
68B	1	100	CWDO	III	FRTH	REH20		PS
138B	1	100	NAOH	III	FRTH			PS
19A	1	100	NONE	SL	FRTH			PS
19B	1	100	NONE	SL	FRTH			PS
30	4	100	NONE	SL	FRTH	STIR		100G
92	4	100	NONE	SL	FRTH			PS
93	4	100	NONE	SL	FRTH			PS
94	4	40	CWDO	SL	FRTH			PS
95	4	40	DH20	SL	FRTH			PS
104	4	20	CWDO	SL	FRTH			PS
105	4	40	CWDO	SL	FRTH			PS
106	4	60	CWDO	SL	FRTH			PS
107	4	80	CWDO	SL	FRTH			PS
108	4	100	NONE	SL	FRTH			PS
135B	BE	80	DH20	ST	FRTH	COMP		PS
136B	BE	80	NAOH	ST	FRTH	COMP		PS
109	2	127	NONE	WSL	FRTH	COMP		PS

LOG OF SETTLING VESSELS ACCORDING TO #,COMPOSITION AND TREATMENT

SV#	SL from	NomSL Conc.	DIL.	So Type	Treat 1	Treat 2	Treat 3	SV Type
110	2	143	NONE	WSL	FRTH	COMP		PS
111	2	178	NONE	WSL	FRTH	COMP		PS
112	2	234	NONE	WSL	FRTH	COMP		PS
127	4	100	NONE	SL	HEAT			100G
128	4	100	NONE	SL	HEAT	HCL		100G
19	1	100	NONE	SL	NONE			PS
142	4	100	NONE	SL	NONE			1G
143	4	100	NONE	SL	NONE			TLC
144	4	100	NONE	SL	NONE			TLC
131	BE	5	DH20	ST	NONE			1G
132	BE	5	NAOH	ST	NONE	.01%		1G
133	BE	5	NAOH	ST	NONE	.02%		1G
134	BE	5	NAOH	ST	NONE	.04%		1G
A	1	100	NONE	WSL	NONE			2MG
12	2	100	NONE	WSL	NONE			1G
103	1	100	DH20	CSOD	RECON			100G
43	1	100	DH20	I	RECON			PS
44	1	60	DH20	I	RECON	DIL		PS
45	1	40	DH20	I	RECON	DIL		PS
46	1	20	DH20	I	RECON	DIL		PS
47	1	5	DH20	I	RECON	DIL		PS
58	1	100	CWDO	I	RECON			PS
59	1	60	CWDO	I	RECON	DIL		PS
60	1	40	CWDO	I	RECON	DIL		PS
61	1	20	CWDO	I	RECON	DIL		PS
48	1	100	DH20	II	RECON			PS
49	1	60	DH20	II	RECON	DIL		PS
50	1	40	DH20	II	RECON	DIL		PS
51	1	20	DH20	II	RECON	DIL		PS
52	1	5	DH20	II	RECON	DIL		PS
63	1	100	CWDO	II	RECON			PS
64	1	60	CWDO	II	RECON	DIL		PS
65	1	40	CWDO	II	RECON	DIL		PS
66	1	20	CWDO	II	RECON	DIL		PS
82	1	100	MEOH	II	RECON			PS
83	1	60	MEOH	II	RECON	DIL		PS
84	1	40	MEOH	II	RECON	DIL		PS
85	1	20	MEOH	II	RECON	DIL		PS
86	1	5	MEOH	II	RECON	DIL		PS
137	1	100	NAOH	II	RECON	REH20		100G
139	1	100	MEOH	II	RECON	REH20		100G
53	1	100	DH20	III	RECON			PS
54	1	60	DH20	III	RECON	DIL		PS
55	1	40	DH20	III	RECON	DIL		PS
56	1	20	DH20	III	RECON	DIL		PS
57	1	5	DH20	III	RECON	DIL		PS
68	1	100	CWDO	III	RECON			PS
69	1	60	CWDO	III	RECON	DIL		PS
70	1	40	CWDO	III	RECON	DIL		PS
71	1	20	CWDO	III	RECON	DIL		PS
72	1	5	CWDO	III	RECON	DIL		PS
73	1	15	DH20	III	RECON	DIL		PS
74	1	10	DH20	III	RECON	DIL		PS

EXPLOGTREAT (MR).4

LOG OF SETTLING VESSELS ACCORDING TO #, COMPOSITION AND TREATMENT

SV#	SL from	NomSL Conc.	DIL.	Sol Type	Treat 1	Treat 2	Treat 3	SV Type
120	1	100	DH20	III	RECON	HEAT		100G
138	1	100	NAOH	III	RECON	REH20		100G
151	1	40	CWDO	III	RECON	DIL		100G
152	1	40	CWDO	III	RECON	DIL	NAOH	100G
158	1	40	DH20	III	RECON	DIL	NAOH	100G
102	1	100	DH20	SLE	RECON			100G
159	1	100	NAOH	SLE	RECON	REH20		100G
114	1	100	DH20	SLEA	RECON			100G
115	1	100	CWDO	SLEA	RECON			100G
162	5	100	NAOH	SLFD	RECON	REH20		100G
190	5	100	CWDO	SLFD	RECON			100G
191	5	100	DH20	SLFD	RECON			100G
56A	1	20	DH20	III	REH20	RESET		PS
73A	1	15	DH20	III	REH20	RESET		PS
152A	1	40	CWDO	III	REH20	RESET		
129A	4	40	NAOH	SL	REH20	RESET		
99	1	100	DH20	CSOD	SWEL			100G
100	1	100	DH20	I	SWEL			100G
98	1	100	DH20	SLE	SWEL			100G
91	4	40	DH20	DEC	UF			100G
13	2	100	NONE	WSL	VIBES			1G

APPENDIX 2

Discussion of Batch Settling Experiments from March 1989 Progress Report

BATCH SETTLING EXPERIMENTS OF TAILINGS SLUDGE FROM THE HOT WATER EXTRACTION OF OIL SANDS

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ABSTRACT

The settling behaviour of tailings sludges and sludge solids from which organics were extracted by solvents was studied. The settling of tailings sludges is very slow, indicating that the samples primarily consolidate under the buoyed weight of the solids. The rate of settling was of the order of 0.001 cm/hr and the corresponding solid flux was about 10^{-6} cm/hr. This slow rate is attributed to an internal or gel-like structure. The settling rate is substantially improved by diluting the solids with sludge water below 0.075 volume concentration (which corresponds to approximately 10% by weight).

The settling of the sludge solids is enhanced substantially by treating the solid surface matrix with different solvents. These samples reach the consolidation stages after 20 days at the original solid concentration (28% wt), whereas sludge itself did not consolidate until approximately one year. Apparently, at the consolidation stage the original sludge forms a structure different from that of organic cleaned solids. The solid concentration of the former is 0.15 and the latter 0.20 volume fraction (the original concentration was 0.125).

INTRODUCTION

Oil production from the oil sands in Alberta has been economically feasible since the development of the Clark hot water process (1). One of the major problems of the exploitation of the mineable oil sands is the ultimate disposal of tailings that result from the hot water separation process. The oil sands tailings stream is an aqueous suspension of sand, clays, residual bitumen and naphtha at pH between 8 and 9. The proportion of components varies upon the oil sands composition. The clays present in the tailings are composed mainly of kaolinite and illite. Heavy metals such as Ti, Zr, Fe,V,Mg, Mn, Al, Pb, Zn, Nb and Mo have also been detected in the tailings (2,3) . Various types of dissolved and clay-associated organics, besides residual bitumen, are found in tailings. The majority are organic acids and polyphenolic aromatic compounds (4).

Among organic acids detected are two classes of surfactants: carboxylic and sulphonic acids (5,6,7). Both of these classes, which are generated by the addition of sodium hydroxide to the tar sands and hot water mixture, aid in the extraction of bitumen in the hot water process (7). However, the same surfactant properties that aid bitumen separation adversely affect settling of clays in tailings (8).

It is important to know why oil sands tailings is such a stable suspension. Several authors have shown that soluble organic surfactants such as sulphonic and carboxylic acids disperse clay particles creating a stable suspension in the pond sludge (6,9,10,11). A stable dispersion could also be formed as a result of repulsive forces due to the high negative surface charges of the clay particles (12,13.14,15,16). It is also possible that bound organics on clay particles may link with bitumen in tailings and thus help to create a stable suspension, reducing the ability of the oil sands tailings to consolidate (17,18,19,20). A number of treatments have been proposed to remedy this problem. These treatments have included chemicals, geotechnical methods, physical methods and process modifications. None of these methods has been commercially developed because of high operational costs.

In the present work, the settling behaviour of tailings pond sludge, which is very similar to concentrated flocculant suspensions widely reported in the literature (21,22,23), is discussed. The effects of dilution of the sludge in sludge water, and of solids cleaned with different solvents and dispersed in sludge water are also presented. The settling rate of solids in the tailings pond sludge can be increased to some extent by solvent treating the solid surfaces.

THEORETICAL BACKGROUND

All steps of the process are profoundly affected by interfacial phenomena like van der Waals or London forces, if not overpowered by electrostatic repulsion (zeta potential) or hydrodynamic shear which can cause particles to adhere on contact. The batch settling curves of suspensions are divided into three types according to their initial concentrations. At high dilutions there exists no visual interface, and such a sedimentation of suspensions is called "free settling". In this concentration range particles are far apart and they settle individually (or independently) at different velocities in Stokesian flow. As solid concentration is increased and particles are crowded closer together, a sharp interface between settling suspension and clear liquid (clarification) appears. This sedimentation is called "zone settling or hindered settling". There is no unique concentration marking a transformation from the Stokesian-type region into zone settling. If the concentration is higher, the sedimentation is divided into another type which, for historical reasons, is called "compression settling or compaction". In this case the particles may form a structure(s) so firm that they develop compressive strength. In order to compact the structure to higher solids concentration, a squeeze must be applied on it.

For mathematical reasons, batch sedimentation can be divided into three zones depending upon the position of the upper and lower phase boundaries as shown in Figure 1. These are generally called:

- the constant rate section,
- the first falling rate zone, and,
- the second falling rate zone.

The constant rate zone ends when the upper boundary (which separates the clarification and settling zones) ceases to fall linearly. The end is marked by the intersection of a characteristic straight line emanating from the initial layer sediment and the locus of the upper phase boundary. At this point, the sediment starts to affect the settling rate of the upper interface and as a consequence the settling rate ceases to decay linearly. The first falling rate period ends when the upper and lower phase boundaries merge. At that point, all of the particles are incorporated in the compressible sediment (or consolidation stage). The second falling rate period involves squeezing of liquid out of the sediment under the force of the buoyed weight of solids.

Kynch's (24) well-known theory of sedimentation is based on the assumption that the settling rate at any point in a column of sludge is a function only of the concentration at that point; i.e. $u = u(C)$. So according to this theory the relationship between settling rate and particle concentration can be deduced from the observation on the fall of the upper boundary of the suspension. The mathematical relationships are best demonstrated by displaying a settling curve as shown in Figure 2. A tangent drawn to the settling curve at any point "a" will intercept the H axis at some value H_i. It will intercept the time axis at some value t_i. What Kynch deduced was that, under the assumptions of the model, the solids concentration just under the upper boundary (or interface) at point "a" would be:

$$C_a = C_o H_o / H_i \qquad (1)$$

where C_o and H_o are the initial solid concentration and the initial height respectively.

The settling rate of solids just below the interface is the subsidence rate of the interface. Therefore:

$$U_a = -dH/dt|_a = H_i / t_i$$

So, the flux of solid particle is

$$U_a C_a = C_o H_o / t_i \qquad (2)$$

Equations (1) and (2) give the settling flux for every concentration that propagates to the surface in the batch test. From these, a settling flux curve versus concentration C_a can be constructed, and from it, the flux capacity of a steady-state thickener can be determined.

EXPERIMENTAL PART

a. Source and Analysis of Sludge

The experiments were carried out using a subsample of a 2000 gallon sample of sludge that was collected from Syncrude's pond in August 1986. This material was then stored in a tank at the Syncrude Research Laboratory. Six pails of 5 gallons each were taken from the tank and the samples were mixed for 24 hours. During the mixing, air was introduced into the sludge resulting in bitumen floating on the surface. As consequence, the samples may be low in bitumen content. Before the samples were used for batch settling experiments, they were filtered through a 250μm screen to remove large pieces of extraneous material (wood, roots, etc). Table 1 shows the composition of the 6 pails. With the exception of pail #2 and #3, all analyzed within a narrow range, indicating an adequate mixing and homogenization before the pails were filled. Table 2 shows the particle size distribution of a typical sample.

In order to obtain a water analysis, which is given in Table 3, the water was separated from the solids by centrifugation, and filtered to remove visible oil. Hereafter, this water will be denoted as "sludge water".

b. Preparations of Solids Fractions - Cleaning with Solvent

Approximately 10 L of sludge were centrifuged at 10,000 rpm for 1 hour. The separation produced roughly 8 L of oily water and 4 Kg of oily solids. The solids were then cleaned as follows:

I- Toluene/Isopropylalcohol (IPA)

Approximately 2 Kg of oily solids were initially cleaned using a 50/50 toluene/IPA mixture to remove water and oil. The solids were then shaken with the solvent mixture, allowed to settle and the solvent removed by decantation. The solids were split into three portions. Each portion was further cleaned with the same solvent mixture and centrifuged until clean supernatant was obtained. Then, the samples were air dried to remove any remaining solvent. The batches of each portion were combined and homogenized by dispersion in deionized water and freeze-dried, and designated as Solids I.

II- Toluene/IPA + Methylene Chloride ($MeCl_2$)

Two portions of Solids I were cleaned with a total of 4 L of methylene chloride by an identical procedure to that for Solids I. This sample was designated as Solids II.

III- Toluene/IPA + $MeCL_2$ + Methanol (MeOH).

One of the methylene chloride portions was additionally cleaned with a total of 2 L of methanol using the same procedure as above. This sample was designated as Solids III.

The total organic carbon (TOC) content of the different solids was determined by Leco carbon analyzer. The results are shown in Table 4. It shows that the toluene/IPA mixtures removed about 75% of the organic carbon from the sludge solids. The solids after extraction by the additional solvents appear to contain about the same amount of organic carbon; however, a finite amount of organic material was actually extracted in arriving at Solids II and III. The only explanation for this observation is an incorporation of the $MeCl_2$ and MeOH into the solid matrix (25). More studies are required to determine the changes which occur in the solids as a result of solvent treatment. These studies will include the use of SEM and XRD techniques.

The samples were homogenized, poured into columns and the height of the interface between the clarification zone and the settling zone was measured as a function of time. The lower interface between sediment and the settling zone was not visible enough to be measured, so unfortunately the growth of the sediment is not reported here. Table 5 shows the experiments that were carried out. The experiments can be divided into three categories:

(i) sludge diluted in sludge water,
(ii) solids (I,II,III) dispersed in sludge water, and,
(iii) solids (I,II,III) dispersed in deionized water.

RESULTS

Figures 3, 4 and 5 show the results of the batch settling experiments. In these figures, the heights of the upper interfaces at a given time were normalized with respect to the initial heights H_o. As seen in Figure 3, the settling rate of the original sludge is very slow. After 40 days (1000 hours) of settling, the clarification zone has been incremented only approximately 1% with respect to the initial height. By dilution of the sludge in sludge water, the settling of the sludge is substantially incremented. At solid concentration 0.050 (by volume), the rate of settling is relatively fast; after 40 days, the clarification zone has been incremented about 50% with respect the initial height. This figure shows the three typical cases of batch sedimentation experiments regarding the initial concentration of solids:

(i) concentrated flocculent suspension where only consolidation occurs,

(ii) intermediate concentration (for solid concentration less than 0.075), and,

(iii) low concentration, for volume concentration less than 0.025.

It can be seen that initial concentration has a profound effect on the settling behaviour.

Figures 4 show the settling behaviour of Solids (I, II, III) dispersed in sludge water. The settling behaviour of Solids I and II were very similar. In contrast, the settling behaviour of solids III was different compared with that of solids I and II. The Solids III system reached the consolidation stages quite early compared with sludge.

Figures 5 show the results of cleaned solids dispersed in deionized water. Even though these curves are not as smooth as those for the sludge water dilutions, they still ilustrate some general trends. Again, Solids III settled much faster than Solids I and II. Solids III reached the consolidation stage after just one day.

DISCUSSION

The settling behaviour of the sludge samples shown in Figure 3 to 5 were quite complicated because of their nature; a mixture of clays, silica fines, naphtha, oil in water. For solids concentration below 0.075 (volume fraction), the batch settling experiments of sludge showed the three zones outlined above. In the case of Solids I and II dispersed in sludge water (Figure 4) and in deionized water (Figure 5), the batch settling experiments did not show the three characterisrics zones. Specifically, Solids I and II dispersed in deionized water (Figure 5a, b), the interface between the clarification zone and the settling zone did not decay linearly. This was probably due to the initial conditions of homogenization of the sludge samples. Thus, there exists an induction period at the earlier stages of the process that affected the whole settling process.

The settling behaviour of Solids III was quite interesting. As shown in Figures 4c and Figure 5c, the settling was faster than the settling of sludge. Surprisingly the total amount of carbon is not that different compared with Solids I and II as shown in Table 4. It is suspected either that some amount of solvent remained at the solid interface (25) or that the MeOH in some way changed the structure of these solids in sludge water or in deionized water. So, the solvent cleaning procedures of Solids III play a very important role in the settling. For Comparison, Figure 6 shows the results for sludge and Solids I, II, III dispersed in sludge water for a solid concentration of 0.125 which is the actual solid concentration of the original sludge. The settling behaviour of Solids I and II were quite simiiar, indicating that additional cleaning of solids I with methylene chloride did not change the structure of the system. As mentioned earlier, the settling of original sludge was very slow and this behavior has been suggested to result frm a gel-like structure of the sludge (26). Apparently, this gel-like structure was modified when the solids were cleaned with different solvents. The final concentration of the solids ;i.e. the concentration at the consolidation stage, also depended on the way that the solids were treated. For example, for sludge the eventual concentration of solids was approximately 0.15 and for Solids III in sludge water and in deionized water was about 0.2. As consequence, Solids III in both sludge water and in deionized water formed a more compact solids composition than sludge.

Figure 7 shows the solid flux (initial) as a function of the solid concentration. The behavior of Solids I and II were quite similar as shown in this figure, in good agreement with settling data shown previously. As consequence, this plot indicates that the electrical surface properties of Solids I and Solids II are very similar. On the other hand, the settling behavior of sludge solids differed from the settling behavior of Solids I or II. At solid concentration below 0.075 the solid fluxes for sludge solids is higher than those observed for Solids I or II. In contrast, at solid concentration above 0.075 the solid fluxes for sludge solids was less than those observed for Solids I or II. This behavior of solid sludge is due apparently to the formation of a gel-like structure.

As showed earlier, the settling behavior of Solids III was quite fast and different compared with other solids. This trend is also evident in Figure 7. The solid flux of Solids III was quite high, about 3 order of magnitude higher than Solids I or Solids II. THis behavior indicates that the electrical surface properties of Solids III were sustantially modified during additional cleaning with solvents.

CONCLUDING REMARKS

The results of the batch settling experiments can be summarized as follows:

- the rate of settling of sludge is very slow, approximately 0.001 cm/hr. The flux is also very slow, of the order of 10^{-4} cm/hr. The slow settling is thought to be due primarily to the gel-like structure formed by the sludge. As a consequence, only consolidation of the system occurs.

- the rate of settling of sludge can be improved by dilution with sludge water. For solids concentrations below 0.050 (this magnitude corresponds to approximately 10% by weight), the settling curves show the three settling zones charateristic of flocculant suspensions. The final solids concentration at consolidation stages turned out to be between 0.12 to 0.15 depending on the initial concentration.

- The settling of solvent cleaned solids is faster than the settling of sludge. Specifically, the settling of solids III in sludge water is shown in Figure 4c and 7. The solid flux is about 10^{-2} cm/hr, which is about two orders of magnitude faster than the settling of sludge.

REFERENCES

1. F.W. Camp, "Processing Athabasca Tar Sands-Tailings Disposal", Can. J. Chem., 55, 581(1977).

2. J.W. Kramers and R.A.S. Brown, "Survey of Heavy Minerals in the Surface-Mineable Area of the Athabasca Oil Sand Deposit", CIM Bull., 69(776), 92(1976).

3. L.W. Trevoy, R. Schutte and R.R. Goforth, "Development of the Heavy Minerals Potential of the Athabasca Tar Sands", CIM Bull., 71(791), 175(1978).

4. L.G. Hepler, C. Dobrogowska and K. Karperski, "Water Soluble Substances From Heavy Oils and Bitumen", in Oil in Fresh Water: Chemistry, Biology, Countermeasure Technology, J.H. Vandermeulen and S.E. Hrudey eds., Pergamon Press pp. 3 (1979).

5. L.H. Ali, "Surface Active Agents in the Aqueous Phase of the Hot Water Flotation Process for Oil Sands", Fuel, 57, 357(1978).

6. M.B. Hockins and G.W. Lee, "Effect of Chemical Agents on Setting Rates of Sludges from Effluents of Hot Water Extraction of Athabasca Oil Sands", Fuel, 56, 325(1977).

7. L.L. Schram and R.G. Smith, "Two Classes of Anionic Surfactants and Their Significance in hot Water Processing of Oil Sands", in Proceedings of the 35th Canadian Chemical Engineering Conference, Calgary, Alberta, Volume 1, 189(1985).

8. J.G. Speight and S.E. Moschopedis, "Surface and Interfacial Phenomena Related to the Hoy Water processing of Athabasca Oil Sands", Alberta Research Council Information Series 86 (1980).

9. H.L. Erskine, "Separation of Clay and Mineral from Heavy Oil Production", in The Future of Heavy Crude and Tar Sands, R.F. Meyer, J.C. Wynn and J.C. Olson eds. pp. 519(1982).

10. S.E. Moschopedis, J.F. Fryer and J.G. Speight, "Water-Soluble Constituents of Athabasca Bitumen", Fuel, 56, 109(1977).

11. S. Levine and E. Sanford, "Clay-Bitumen Interactions to Tar Sand Processing", in Proceedings of the 30th Canadian Chemical Engineering Conference, Edmonton, Alberta, Volume IV: Oil Sands, Coal and Energy Modelling, S.E. Wanke ed. CSChE Publications, 1112(1980).

12. R.N. Young and A.J. Sethi, Mineral Particle Interaction Control of Tar Sand Sludge Stability", J. Can Petroleum Technology, 17(4), 76(1978).

13. N.S. Srinivan, J.J. Spitzer and L.G. Hepler, "Electrophoretic Properties of Oil Sands Tailings and Constituent Clays in Aqueous Suspensions", J. Can Petroleum Teccnology, 21(4), 25(1982).

14. E.S. Hall and E.L. Tollefson, "Use of Hard Water for Treatment of Oil Sand Tailings", AOSTRA J. Res., 1, 43 (1984).

15. K.F. Schulz and D.N. Morrison, "Great Canadian Oil Sands Tailings Disposal Problem", Alberta Research Council Open File Report 1973-38, pp 10(1973).

16 S.Lane, "Lime Coagulation and Stabilization of Total Oil Sands Tailings", in Preprints of the 34th Annual Technical Meeting of the Petroleum Society of the CIM, Petroleum Society of the CIM Paper N_o 83-34-33, 1983.

17. M.A. Kessick, "Ion Exchange and Dewaterability of Clay Sludges", Int.J. Mineral Proc., 6, 277(1980).

18. M.A. Kessick, "Complex Acids and Their Role in the Stability of Oil Sands Clay Tailings", Clays and Clay Minerals, 27(4), 301(1979).

19. B. Kratochvil, C. Maitra, D.S. Montgomery and O.P. Strausz, "Chemical and Mineral Characterization of the Bitumen-Free Athabasca Oil Sands Related to the Bitumen Concentration in the Sand Tailings from the Syncrude Batch Extraction Test", AOSTRA J. Res., 2, 59(1985).

20. M.A. Kessick, "Structure and Properties of Oil Sand Clay Tailings", J. Can. Petroleum Technology, 18(1), 49(1979).

21. B. Fitch, "Sedimentation of Flocculent Suspensions: State of the Art", AIChE J. 25(6), 913(1979).

22. D.C-H. Cheng, "Sedimentation of Suspensions and Storage Stability", Chem. & Ind., May 17, 407(1980).

23. A. S. Michaels and J.C. Bolger, "Settling Rates and Sediment Volumes of Flocculated Kaolin Suspensions", I & EC Fundamentals, 1, 24(1962).

24. G.J. Kinch, "A Theory of Sedimentation", Trans. Faraday Soc., 48, 166(1952).

25. C.M Cerda, B.J. Fuhr and K.C. Pongar, "Fundamental Properties of Tailings Sludge from Hot Water Extraction of Oil Sands", progress report, August 1988.

26. C.M. Cerda, B.J. Fuhr, K.J. Pongar and R. Schutte, "Fundamental Properties of Tailings Sludge from Hot Water Extraction of Oil Sands", Progress Report, December 1988.

TABLES

1. Composition of the original sludge samples used during the experiments.

2. Particle size analysis of the sludge solids.

3. The chemical composition of the sludge water.

4. Total organic carbon at the solid sludge matrix.

5. List of experimental runs.

TABLE 1

Analysis of the Sludge Samples

Pail #	wt% Solids	wt% Bitumen	wt% Water
1	27.50	1.95	70.55
2	30.60	2.10	67.30
3	29.20	1.95	68.80
4	27.30	1.75	70.95
5	27.60	1.85	70.55
6	27.95	1.85	70.20

TABLE 2

Particle Size Analysis by Sieve and Coulter Counter and Microtrack

Size (μm)	Cumulative weight %	
	Sieve and Coulter	Microtrack
177	0.7	
150		1.1
125	2.4	
88	5.0	2.2
62.5	7.4	3.1
44.0	10.4	6.1
37.0	11.9	
31.0		12.2
22.0		16.1
20.2	12.4	
16.0	14.3	23.6
12.7	17.4	
11.0		32.5
10.1		21.9
8.0	27.2	
7.8		41.6
6.3	33.0	
5.5		51.3
5.0	40.4	
4.0	47.9	
3.9		64.0
3.2	55.9	
2.8		75.8
2.5	63.5	
2.0	70.4	
1.9		87.3
1.6	78.0	
1.4		95.2
1.3	84.7	
1.0	90.8	
0.8	95.5	
0.6	100	

TABLE 3

Water analysis

pH	8.2
TOC mg/L	92
TIC "	209
Fe "	0.2
Na "	455
K "	9.0
Ca "	6.3
Mg "	4.3
B "	1.9
Cl "	116
SO_4 "	2.4

TABLE 4

Total Amount of Organic Carbon of the Solids

	TOC (wt%)
Original sludge solids	9.71
Solids I (toluene/IPA extracted)	2.60
Solids II (above + $MeCl_2$ extracted)	2.76
Solids III (above + MeOH extracted)	2.75

TABLE 5

List of the Experimental Runs

Run #	Concentration Volume Fraction	Dilution	Solids Type
	Whole Sludge and Dilution		
1	0.125	SW[1]	SS[2]
2	0.100	"	"
3	0.075	"	"
4	0.050	"	"
5	0.025	"	"
6	0.0062	"	"
	Solids Dispersed in Sludge Water		
7	0.125	SW	I
8	0.075	"	"
9	0.050	"	"
10	0.025	"	"

11	0.125	"	II
12	0.075	"	"
13	0.050	"	"
14	0.025	"	"
15	0.125	"	III
16	0.075	"	"
17	0.050	"	"
18	0.025	"	"
19	0.0062	"	"

Solids Dispersed in Deionized Water

20	0.125	H_2O	I
21	0.075	"	"
22	0.050	"	"
23	0.025	"	"
24	0.0062	"	"
25	0.125	"	II
26	0.075	"	"
27	0.050	"	"
28	0.025	"	"
29	0.0062	"	"

30	0.125	"	III
31	0.075	"	"
32	0.050	"	"
33	0.025	"	"
34	0.0062	"	"

[1] SW = Sludge Water

[2] SS = Sludge Solids

FIGURE CAPTIONS

1. Typical batch settling curve showing the three characteristics zones that undergo a suspension during sedimentation.

2. Graphical method for determining the solid concentration and solid flux at time t_a.

3. Settling curves of sludge (solid concentration 0.125) and dilution in sludge water.

4. Settling curves of solids cleaned with different solvents and dispersed in sludge water: a) Solids I, b) Solids II, and c) Solids III.

5. Settling curves of solids cleaned with different solvents and dispersed in deionized water: a) Solids I, b) Solids II, and c) Solids III.

6. Settling curves of sludge ( ), Solids I ( ), II ( ) and III ( ) in sludge water. The solid concentration is 0.125 by volume fraction which corresponds to in situ solid concentration (about 28% by weight).

7. Initial solid fluxes of solids in sludge water for different initial concentrations: ( ) Solids I, ( ) Solids II, ( ) Solids III and ( ) sludge solids.

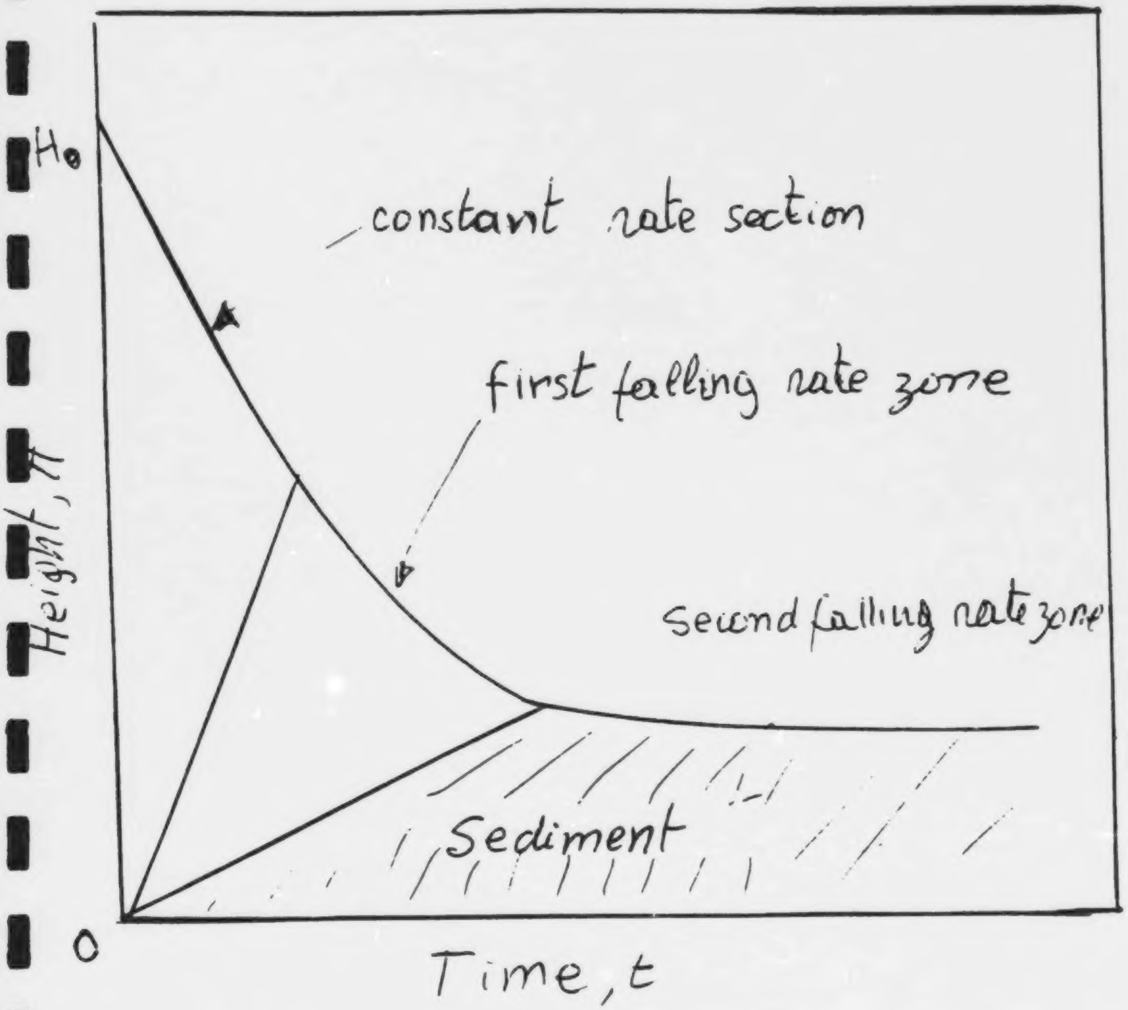


Fig.1. Typical batch settling curve showing the three characteristics zones that undergo a suspension during sedimentation.

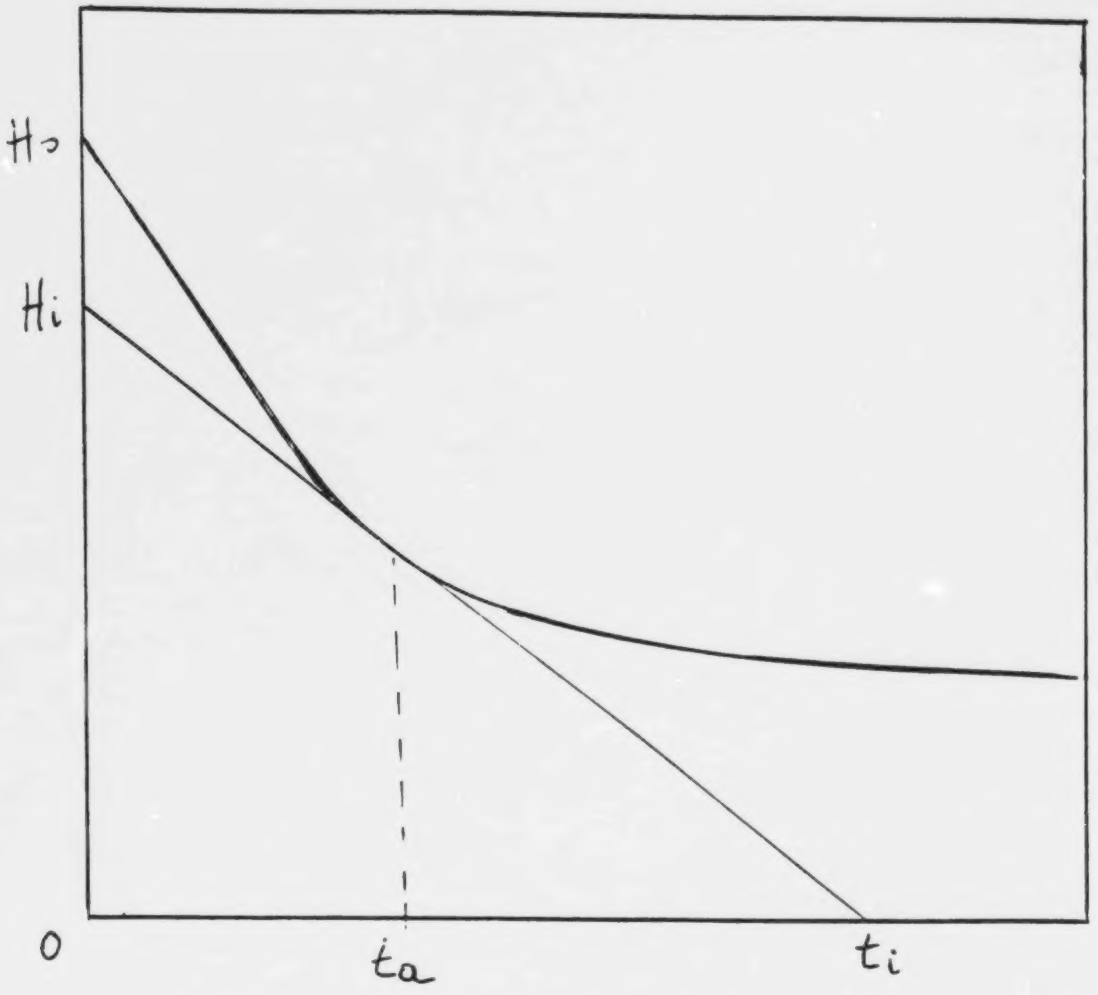


Fig.2. Graphical method for determining the solid concentration and solid flux at time t_a.

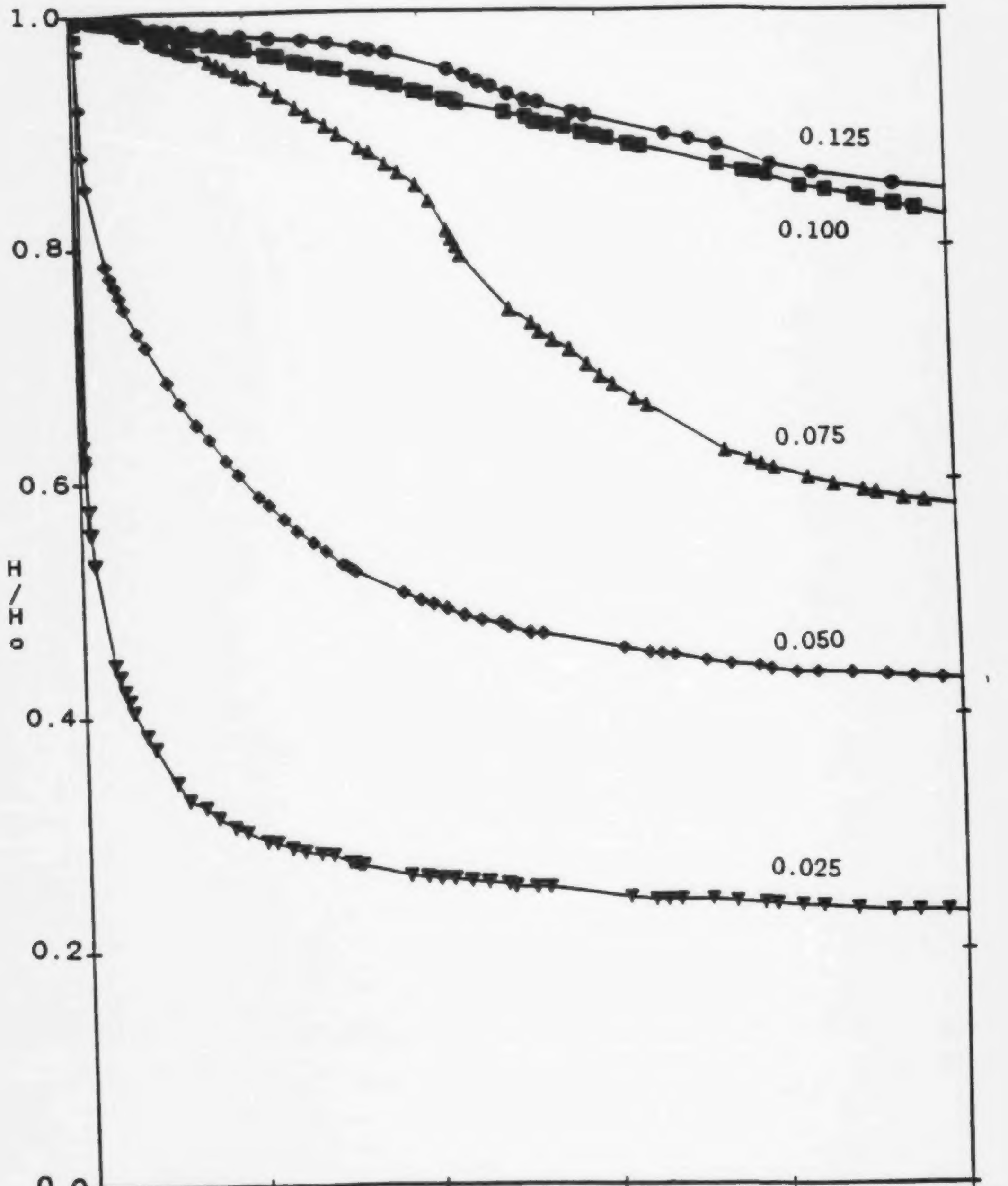


Fig. 3. Settling curves of sludge (solid concentration 0.125) and dilution in sludge water.

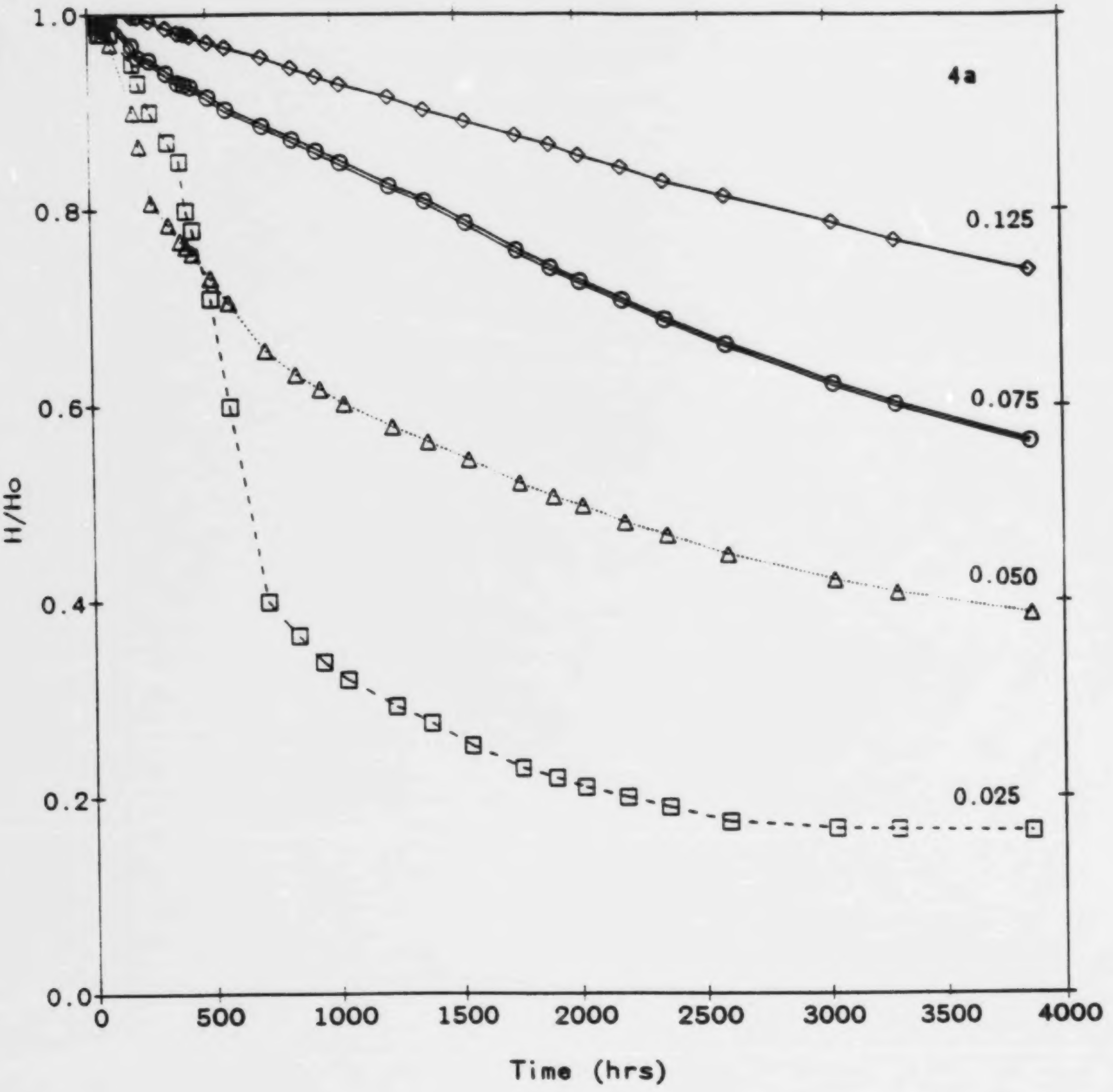
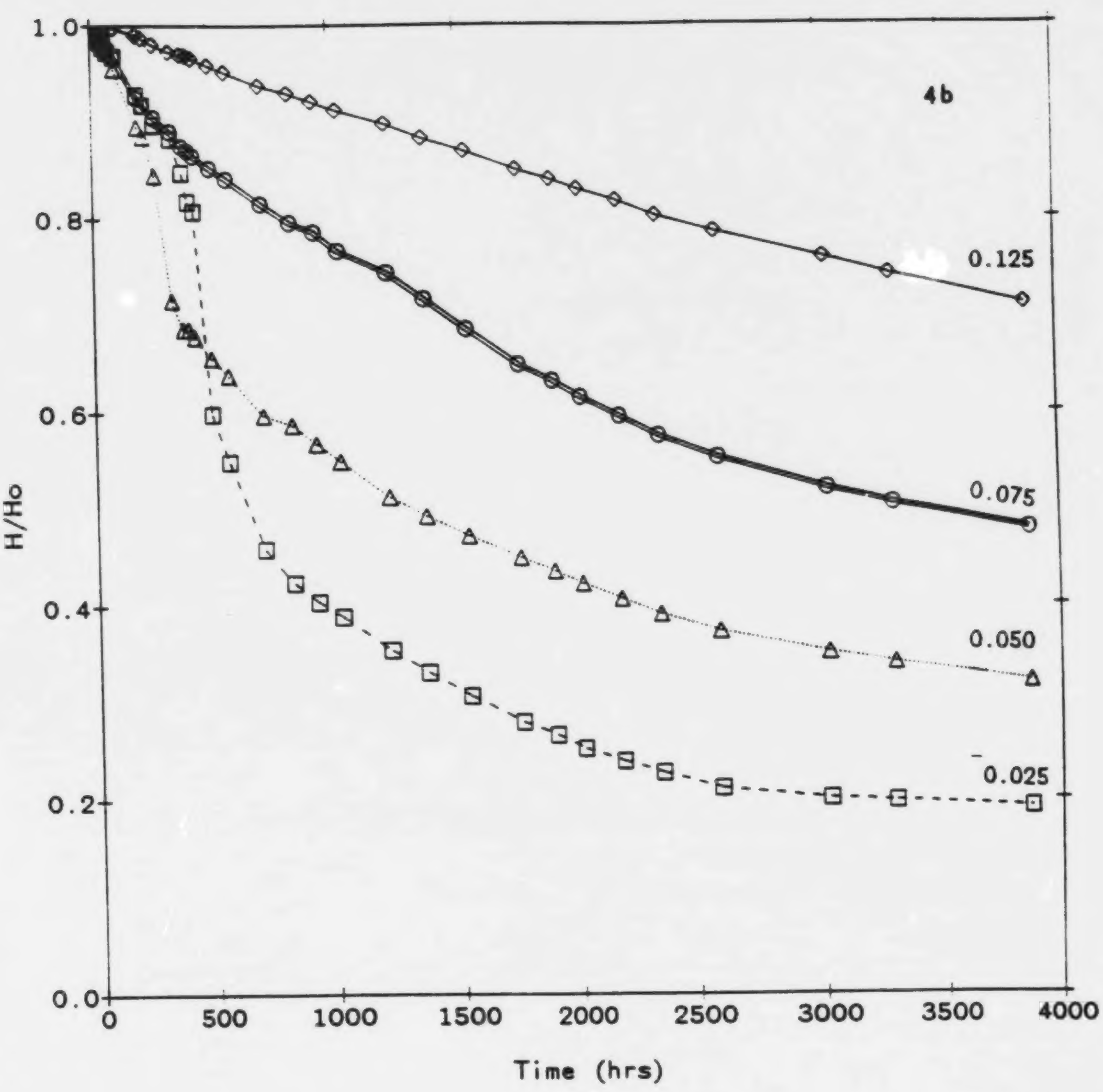
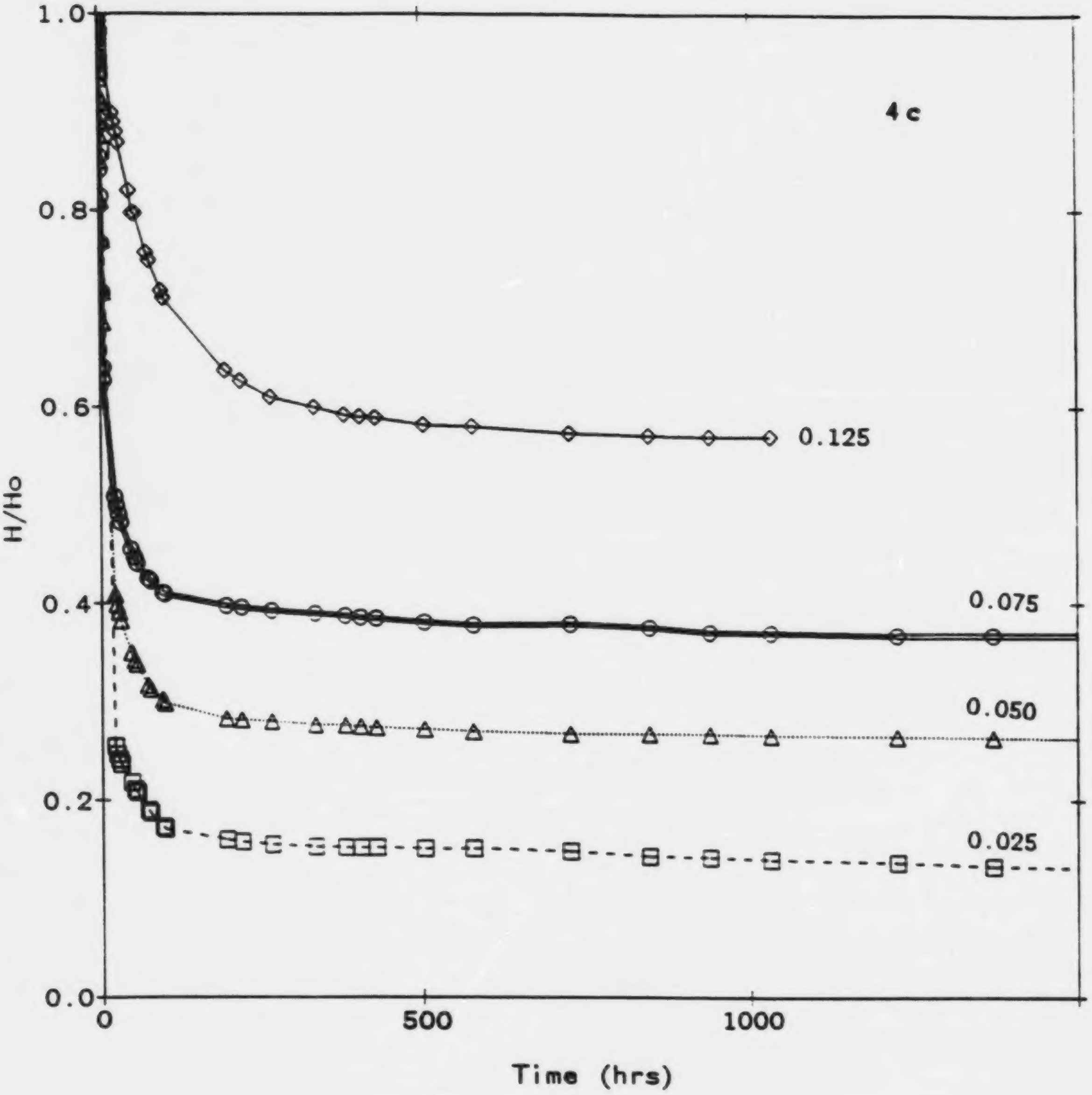


Fig. 4. Settling curves of solids cleaned with different solvents and dispersed in sludge water: a) Solids I, b) Solids II, and c) Solids III.


4b
1.0
0.8
0.6
0.4
0.2
0.0
H/Ho
0
500
1000
1500
2000
2500
3000
3500
4000
Time (hrs)
0.125
0.075
0.050
0.025


4c
1.0
0.8
0.6
0.4
0.2
0.0
H/Ho
0
500
1000
Time (hrs)
0.125
0.075
0.050
0.025

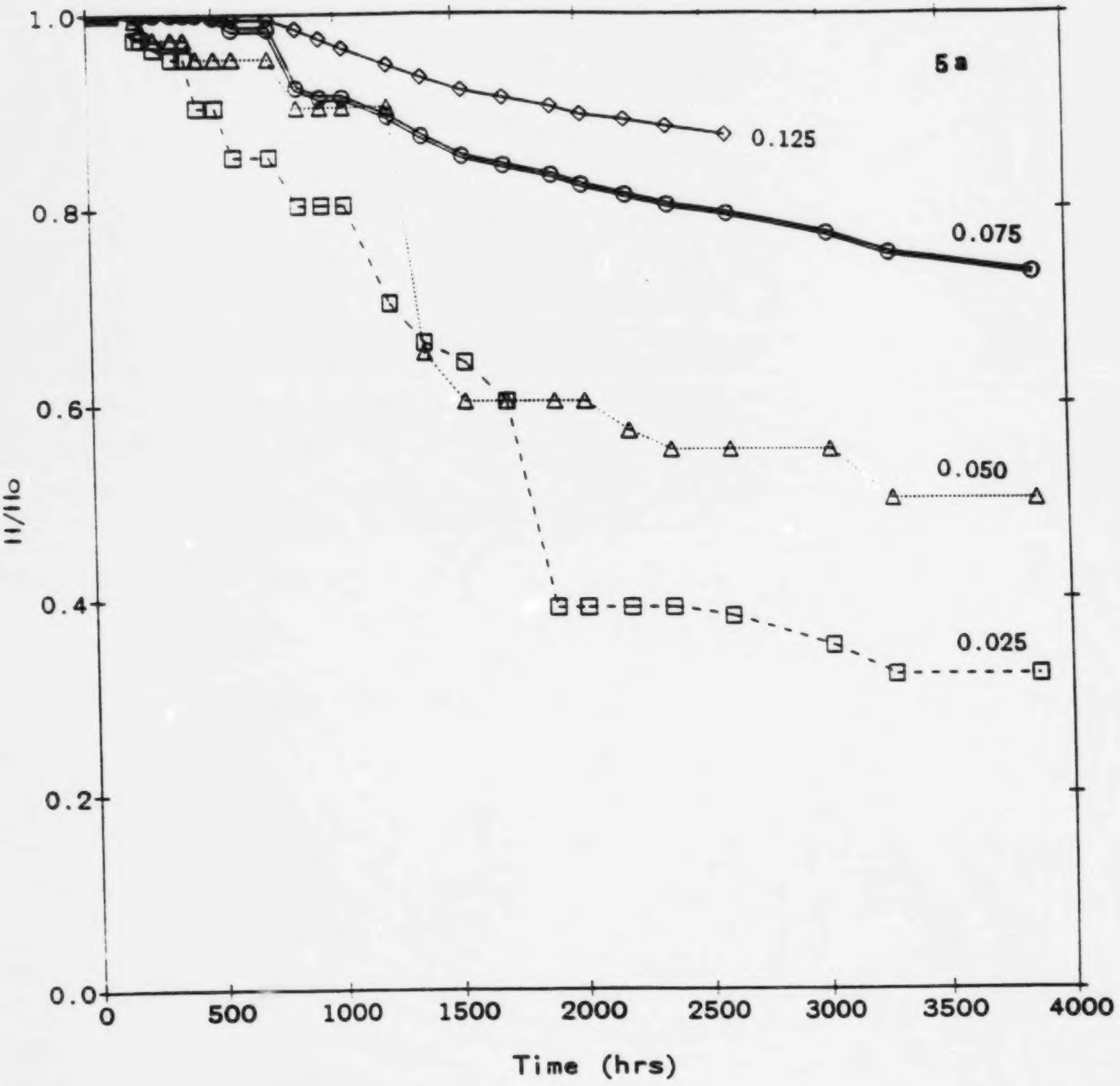
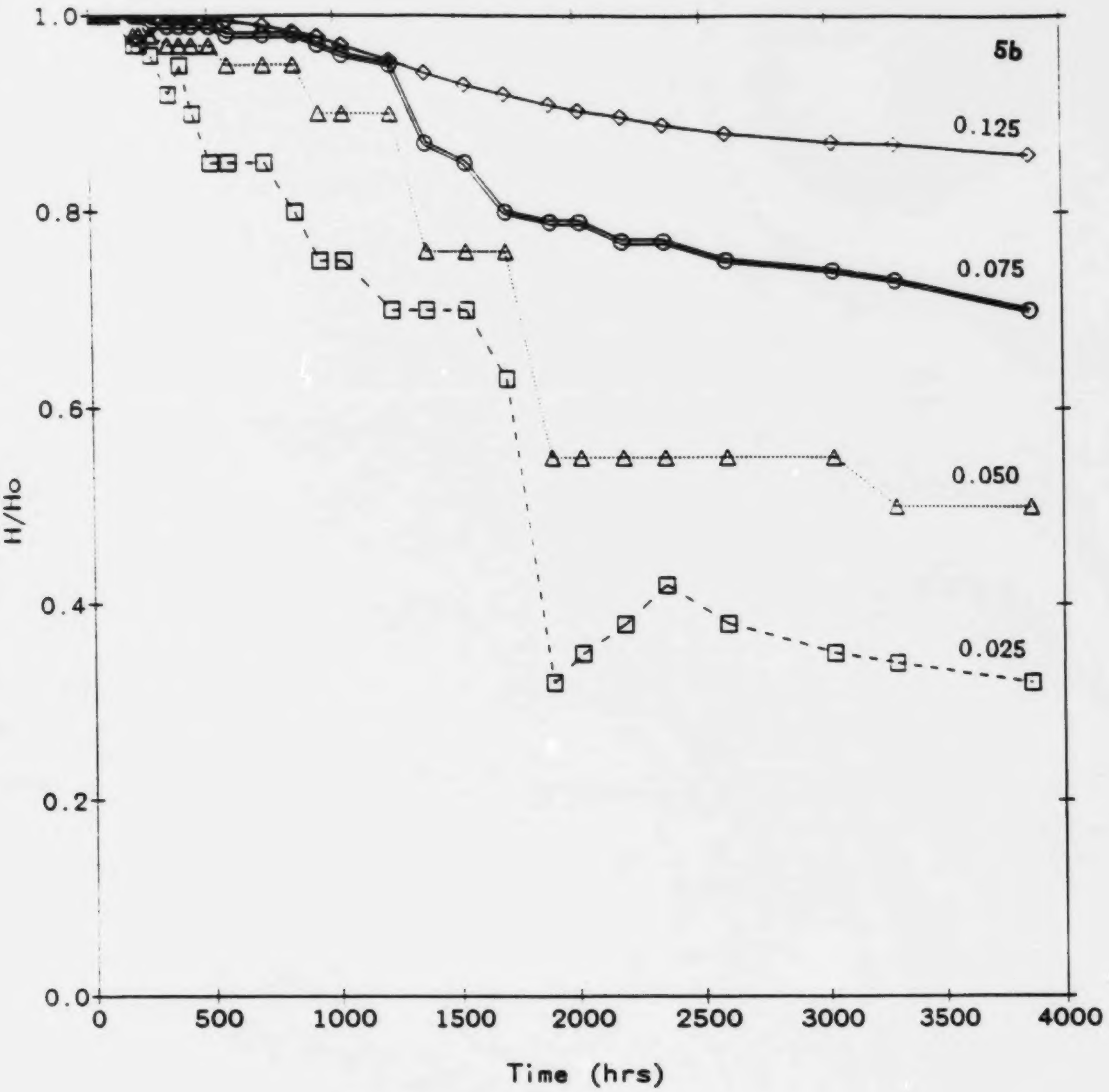
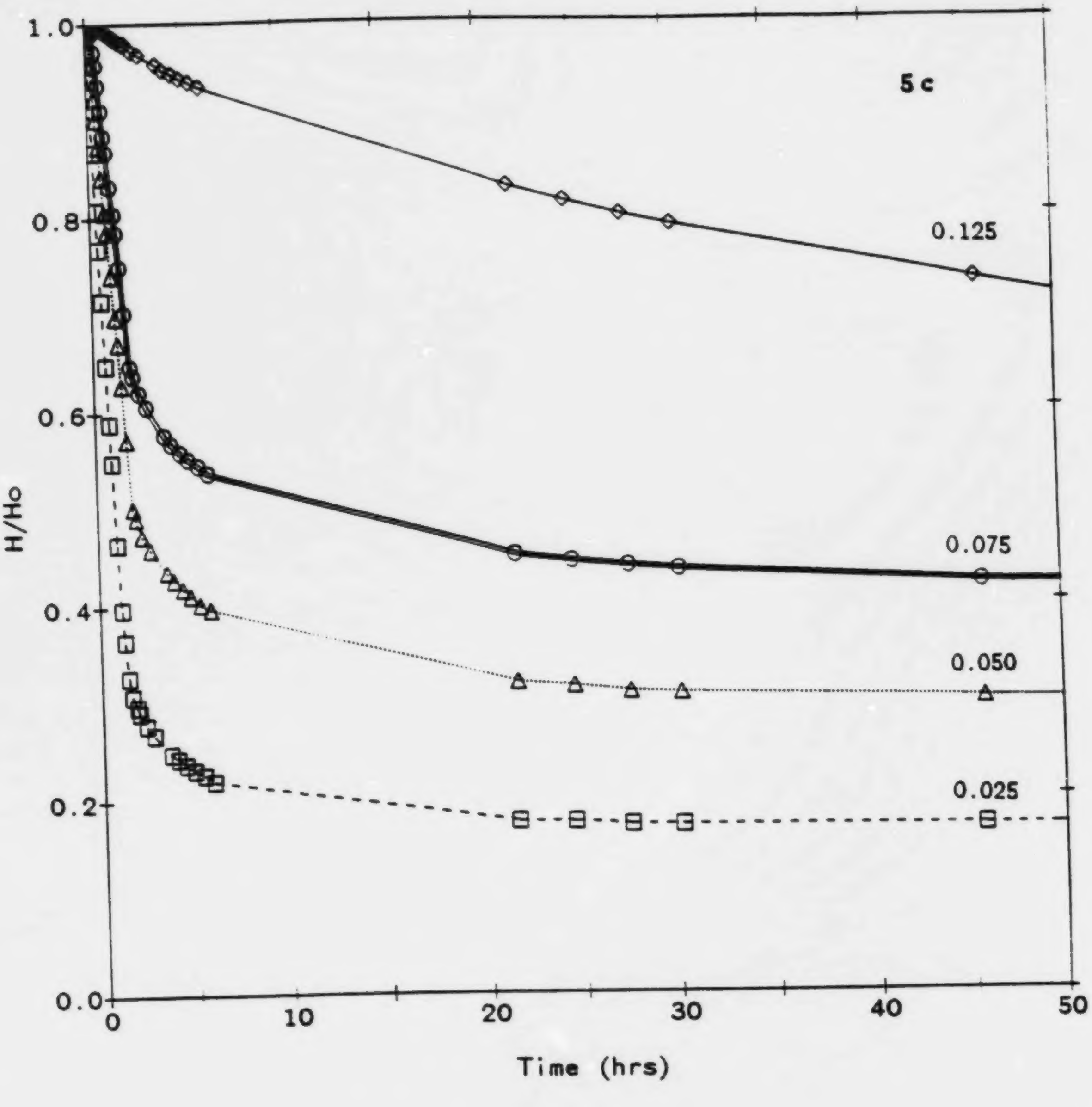


Fig. 5. Settling curves of solids cleaned with different solvents and dispersed in deionized water: a) Solids I, b) Solids II, and c) Solids III.


5b
1.0
0.8
0.6
0.4
0.2
0.0
H/Ho
0
500
1000
1500
2000
2500
3000
3500
4000
Time (hrs)
0.125
0.075
0.050
0.025


5c
0.125
0.075
0.050
0.025
H/Ho
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
Time (hrs)

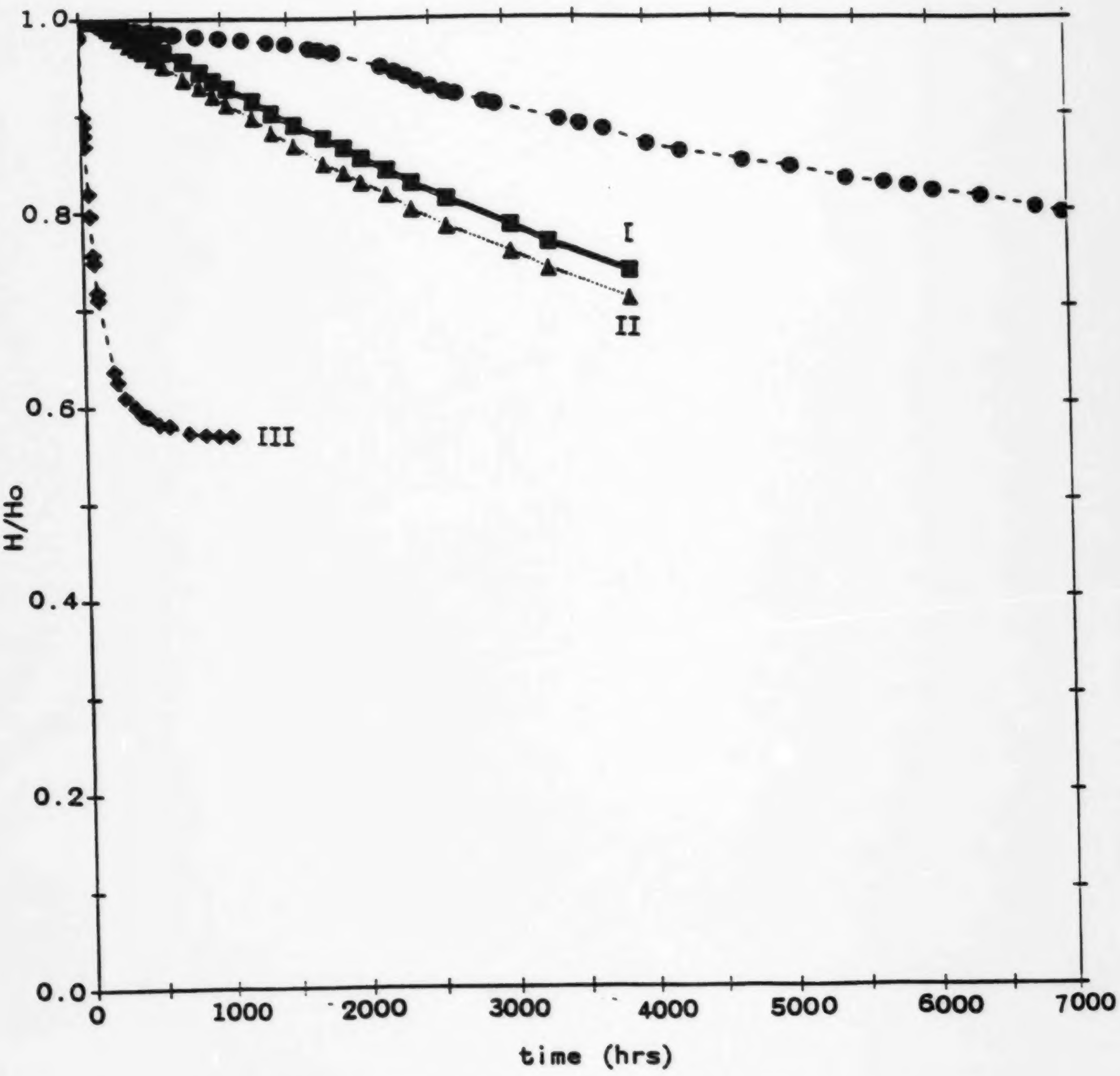


Fig. 6. Settling curves of sludge (●), Solids I (■), II (▲) and III (◆) in sludge water. The solid concentration is 0.125 by volume fraction which corresponds to in situ solid concentration (about 28% by weight).

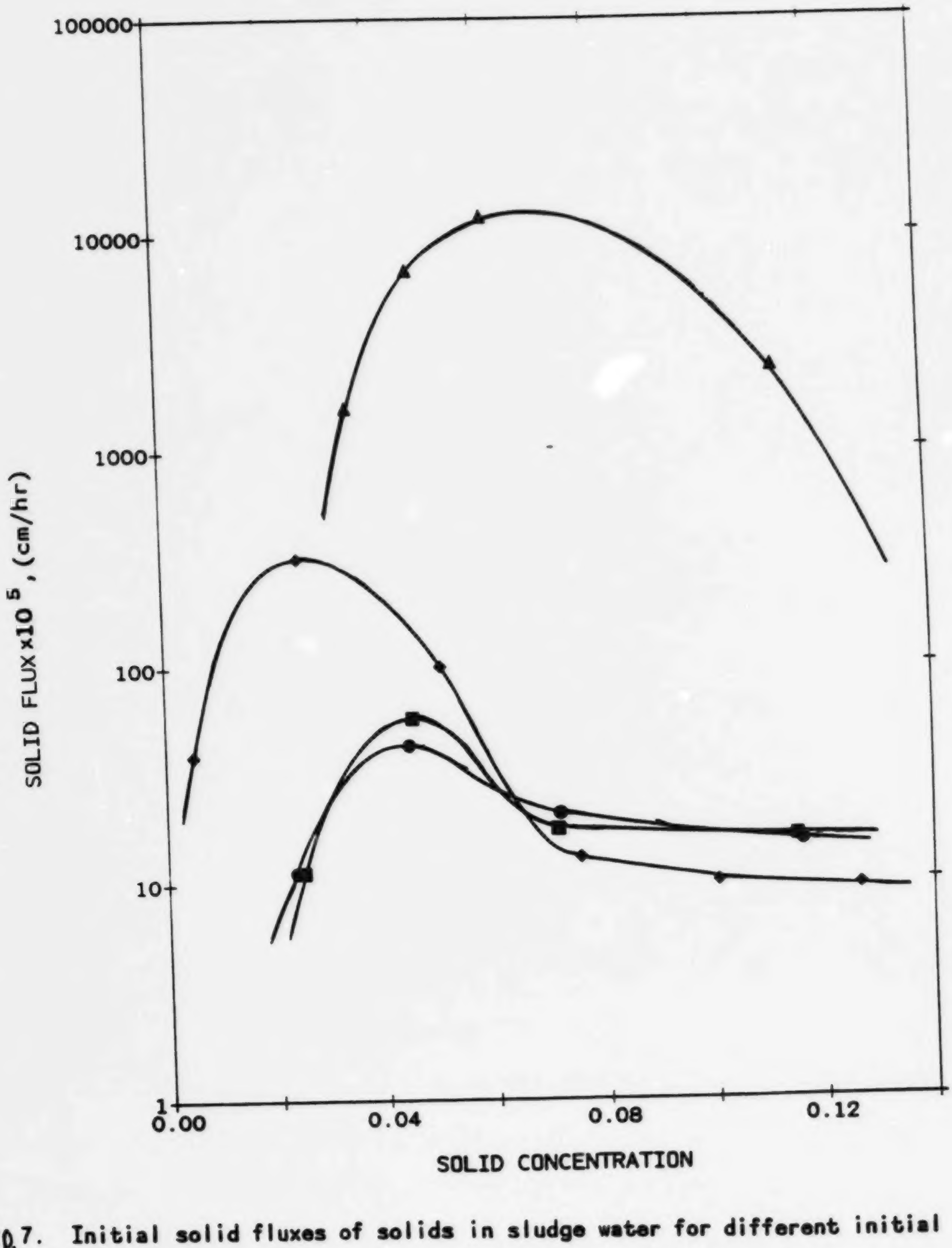


Fig 7. Initial solid fluxes of solids in sludge water for different initial concentrations: (■) Solids I, (●) Solids II, (▲) Solids III and (◆) sludge solids.